

VIII. APPLICABILITY, QUALITY, AND RELIABILITY OF RESULTS

A. INTRODUCTION

To address the applicability, the quality, and the reliability of the results of each of the main Chapters in this report (II through VI), we are including discussions of the purpose and objective of each study relevant to this report as well as the rationale

for the tests conducted. Each of the sections that follows is based on material taken from study plans for the Yucca Mountain Site Characterization Plan (SCP) that were appropriate to topics in this report (Table 36), and each section is, thus, expressed from a point of view prior to actual research.

Table 36. Yucca Mountain Site Characterization Plan (SCP) Studies Relevant to This Report

SCP Number	SCP title	Location in report
Investigation 8.3.1.3.1: . . . on water chemistry . . .		
Study 8.3.1.3.1.1	Groundwater chemistry model	Chp. II
Activity 8.3.1.3.1.1.1	Conceptual model	
Activity 8.3.1.3.1.1.2	Mathematical model	
Investigation 8.3.1.3.4: . . . on radionuclide retardation by sorption . . .		
Study 8.3.1.3.4.1	Batch-sorption studies	
Activity 8.3.1.3.4.1.1	Batch-sorption measurements as a function of solid-phase composition	Chp. IV: A, B
Activity 8.3.1.3.4.1.2	Batch-sorption measurements as a function of sorbing element concentrations (isotherms)	Chp. IV: A
Activity 8.3.1.3.4.1.3	Sorption as a function of groundwater composition	Chp. IV: A
Activity 8.3.1.3.4.1.4	Sorption on particulates and colloids	Chp. V: D
Study 8.3.1.3.4.3	Development of sorption models	Chp. IV: C
Investigation 8.3.1.3.5: . . . on radionuclide retardation by precipitation . . .		
Study 8.3.1.3.5.1	Dissolved species concentration limits	Chp. III
Activity 8.3.1.3.5.1.1	Radionuclide solubility measurements	
Activity 8.3.1.3.5.1.2	Radionuclide speciation measurements	
Activity 8.3.1.3.5.1.3	Solubility modeling	
Study 8.3.1.3.5.2	Colloid behavior	Chp. V: D
Activity 8.3.1.3.5.2.1	Colloid formation, characterization, and stability	
Activity 8.3.1.3.5.2.2	Colloid modeling	
Investigation 8.3.1.3.6: . . . on retardation by dispersive, diffusive, and advective transport . . .		
Study 8.3.1.3.6.1	Dynamic-transport column experiments	
Activity 8.3.1.3.6.1.1	Crushed-tuff column experiments	Chp. V, A
Activity 8.3.1.3.6.1.2	Mass transfer kinetics	Chp. V, A
Activity 8.3.1.3.6.1.3	Unsaturated tuff columns	Chp. V, B
Activity 8.3.1.3.6.1.4	Fractured tuff column studies	Chp. V, C
Activity 8.3.1.3.6.1.5	Filtration	Chp. V, D
Study 8.3.1.3.6.2	Diffusion	
Activity 8.3.1.3.6.2.1	Uptake of radionuclides on rock beakers in a saturated system	Chp. VI, A
Activity 8.3.1.3.6.2.2	Diffusion through a saturated tuff slab	Chp. VI, B
Activity 8.3.1.3.6.2.3	Diffusion in an unsaturated tuff block	Chp. VI, C

B. GROUNDWATER CHEMISTRY MODEL

Purpose and Objectives of Studies

Introduction and objectives

The purpose of the groundwater chemistry investigation is to provide a model of groundwater chemistry at Yucca Mountain that reflects groundwater compositions that will occur as a result of interaction with different chemical environments. The groundwater chemistry model will show the geochemical materials that control the composition of the present groundwater, will support site-characterization activities, and will be used to support the resolution of Performance Assessment Issues 1.1 (Total System Performance), 1.8 (Siting Criteria), and 1.5 (Engineered Barrier Performance). In addition, the groundwater chemistry model will support the geochemistry program by providing actual or simulated data on water composition required by other investigations, studies, or activities.

The groundwater chemistry model is being developed in two phases through the Yucca Mountain Site Characterization Plan (SCP) Activities 8.3.1.3.1.1.1 (Conceptual Model) and 8.3.1.3.1.1.2 (Mathematical Model). The purpose of Activity 8.3.1.3.1.1.1 is to develop conceptual models of groundwater chemistry that isolate the geochemical parameters with the greatest influence on groundwater composition. The purpose of Activity 8.3.1.3.1.1.2 is to develop mathematical models of groundwater chemistry. These models will be based on the conceptual model and will use the important variables and parameters to quantitatively predict the ranges of groundwater composition subject to fluctuations in overall chemical conditions due to changes in the Yucca Mountain environment.

Development of the conceptual model

A preliminary conceptual model of groundwater chemistry will be proposed to provide a qualitative understanding of the geochemical parameters and processes controlling the groundwater composition over time. The effects of chemical parameters and geochemical processes, such as pH, mineralogy, and

sorption, on groundwater composition will be suggested in the preliminary model. Hypotheses about the variables, parameters, and geochemical processes most affecting groundwater composition will be formulated from the preliminary conceptual model. This study suggests several tests of the preliminary model and the hypotheses derived from it that will provide information on specific variables, parameters, and processes and will be used to refine the preliminary model. The behavior of different parameters will be examined by computer codes and tested through detailed experiments, and those parameters that most influence the groundwater composition will be included in a refined conceptual model. The final conceptual model will be the product of this activity and will provide the initial information for development of a mathematical model of groundwater chemistry at Yucca Mountain.

Developing conceptual models of groundwater composition requires a database of the geochemical parameters, variables, and processes that could influence groundwater composition. The database will be developed through tests of hypotheses generated from the preliminary conceptual model, previously published data on groundwater at Yucca Mountain or in the vicinity, and other studies, namely SCP Studies 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone) and 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry). The database will be used with the conceptual model to develop and test the mathematical model in Activity 8.3.1.3.1.1.2. The database will include data and calculations on processes that are important, such as pH, redox conditions, and sorption, as well as the concentrations of aqueous ions such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , F^- , HCO_3^- , Al^{3+} , Mn^{2+} , Fe^{3+} , Fe^{2+} , $\text{SiO}_2(\text{aq})$, and other trace constituents. In addition, data and information on geochemical processes related to groundwater chemistry, such as secondary mineral precipitation, will be included, as will data on mineralogy, petrology, and radionuclide solubility and the array of environmental conditions to be used in the calculations. The information will show the variables and parameters primarily controlling

groundwater composition. It will also show the constituents of least importance to groundwater composition. The completed database with the conceptual model will be the initial input for development of the mathematical model in Activity 8.3.1.3.1.1.2. Relations among data in the database will be further tested by the mathematical model.

Development of the mathematical model

After the conceptual model is completed, the mathematical model will be developed in Activity 8.3.1.3.1.1.2. The relationships between parameters and the results of calculations suggested by the development of the conceptual model cannot be quantified until the important geochemical parameters and processes are identified. Because of this limitation, details of the exact development of the mathematical model can only be supplied as the conceptual model nears completion. The goal of Activity 8.3.1.3.1.1.2 is to produce a mathematical model of groundwater composition that can be used to predict groundwater composition as a result of different chemical environments over time. The model will be used to calculate the results on the basis of input data distributions and on an estimate of the uncertainty in the calculations. The mathematical model will support the calculations of radionuclide retardation that ultimately will be used to support the resolution of Performance Assessment Issue 1.1.

Sources of data for development of models

To develop a conceptual model and a mathematical model of groundwater chemistry, this study will obtain data on major ion chemistry and on other parameters important to groundwater composition. Published reports and other Yucca Mountain Site Characterization Project (YMP) studies (for example, from SCP Study 8.3.1.2.2.7, Hydrochemical Characterization of the Unsaturated Zone) will be used. Data on mineralogy and petrology of rock matrix minerals and fracture minerals will be obtained from Study 8.3.1.3.2.1 (Mineralogy, Petrology, and Chemistry of Transport Pathways), and information on the alteration of minerals will be obtained from Study 8.3.1.3.2.2 (History of

Mineralogic and Chemical Alteration of Yucca Mountain). The mineralogical and petrological data define the minerals present at Yucca Mountain. This information will then be used to evaluate how these minerals control groundwater composition. The alteration history will provide information on the changes in minerals with time and will suggest possible changes in groundwater composition as a result of mineral transformation through time. Information on the kinetics of mineral dissolution and precipitation will be obtained from the literature.

Duffy (1985) showed that the kinetics of mineral transformations are important components to incorporate in the conceptual models for groundwater chemistry because few of the interactions between rock and water at Yucca Mountain are expected to reach true thermodynamic equilibrium. Some rock-water interactions appear to reach states of metastable equilibrium in which solution concentrations are controlled by solid phases that are present for relatively long periods of time. For example, cristobalite may control the activity of silica in Yucca Mountain groundwater even though cristobalite is metastable with respect to quartz.

Data from different studies will be used with groundwater chemistry data to determine the minerals that control groundwater composition, the stability of pH, redox conditions of groundwater at Yucca Mountain, and the composition of the groundwater as a result of interactions between host rocks and different weathering environments over time. Timely exchange of data among these studies will be important so that the groundwater chemistry model can be developed and refined with the most recent data and interpretations gathered from other studies. In turn, the groundwater chemistry model will provide current information on groundwater composition to other studies for their continuing development.

Goals

This study will develop models of groundwater chemistry at Yucca Mountain under different envi-

ronmental scenarios through time. SCP Activity 8.3.1.3.1.1.1 will develop conceptual models of groundwater composition and will evaluate and refine the model through several tests and analyses of the effects of different geochemical processes and parameters on groundwater composition. In Activity 8.3.1.3.1.1.2, the conceptual models will be used to develop a mathematical model that can be used to predict groundwater composition through time when different sets of environmental conditions are imposed on the system.

Objectives for SCP Activity 8.3.1.3.1.1.1

Three objectives must be met before the final conceptual model is complete. These objectives include detailed laboratory tests and use of different computer codes to evaluate different parameters and to calculate chemical speciation. The objectives and related tests are outlined below and discussed in detail later. Similar objectives are developed for Activity 8.3.1.3.1.1.2.

Objective 1: Propose preliminary conceptual model

A preliminary conceptual model of groundwater chemistry will include the effects of different parameters. First, the preliminary conceptual model will consider the composition of groundwater at Yucca Mountain and surrounding areas. These data will be derived largely from published reports, but data from other investigations in the Geohydrology and Geochemistry Overviews (SCP Sections 8.3.1.2 and 8.3.1.3, respectively) will be used as they become available.

The conceptual model will consider the influence of the mineralogy of Yucca Mountain on the composition of groundwater. These data will show the relative importance of different primary minerals and secondary minerals (silicate phases, oxides, and zeolites) in controlling groundwater composition. Information on mineral alteration will also be included in the conceptual alteration of minerals. The information on mineral alteration will be used to suggest dissolution of existing minerals and precipitation of new phases over time.

The preliminary conceptual model will suggest those parameters that could significantly affect groundwater composition. The variables that determine the parameters will also be suggested as major controls on groundwater composition, and the function of HCO_3^- in controlling pH will be considered. The parameters that control pH, redox conditions, mineralogy, sorption, and mineral alteration are considered the main contributors to groundwater composition, but their relative importance remains to be demonstrated. These parameters will be examined in a preliminary conceptual model so that a more thorough conceptual model can be developed.

The conceptual model will include the influence of sorption processes on groundwater chemistry to account for changes in groundwater composition resulting from adsorption and desorption of chemical constituents on different secondary and primary minerals. Information on sorption of radionuclides will also be included to permit modeling of future groundwater compositions that include different concentrations of radionuclides.

Information on the hydrology of the system will be included. Data from hydrologic studies, for example, Study 8.3.1.2.3.2 (Characterization of the Saturated Zone Hydrochemistry), will give information on flow rates through unsaturated and saturated material and will be used by this activity to estimate the rate of change of groundwater composition through time. Groundwater chemistry data will also be used in Investigation 8.3.1.3.7 (Radionuclide Retardation by All Processes) to calculate radionuclide release to the accessible environment.

Preliminary conceptual models will be examined, using the tests listed in the following sections, to refine and simplify the model. These tests of the preliminary model are important for several reasons. First, the test results will isolate the parameters and processes that most influence the water compositions and those that are relatively insignificant. Processes controlling organic concentrations are important to the overall groundwater composi-

tion in some settings but are expected to be less important in this study because of their low concentration at Yucca Mountain.

Second, the information accumulated from these tests will be an important part of the database around which the conceptual models are developed and from which the mathematical models are formulated. This database is currently not complete enough to use for model development, and it must be augmented. The tests described below will provide information on pH control, redox conditions, and rock-water interactions that are important to groundwater composition, and information from Studies 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone) and 8.3.1.2.3.2 (Characterization of the Saturated Zone Hydrochemistry) will complete the database.

Third, the results of the tests will help refine the conceptual model. The conceptual model will integrate information on the important parameters, and those variables that determine them, with existing information on groundwater composition models that will also be examined as the preliminary model is refined. The final conceptual model will then be the initial input for the development of the mathematical model.

Fourth, the sensitivity of the conceptual model will be estimated along with the effects of changes in different parameters or omission of different parameters on predicted groundwater compositions. Information on the sensitivity of the conceptual model to changes in different parameters will be important in the development of the mathematical model.

Objective 2: Test parameters identified in preliminary conceptual models

Test 1: The pH stability of groundwater in saturated and unsaturated zones. This test will evaluate the stability of pH of Yucca Mountain groundwater under different chemical environments. Testing pH stability cannot be conducted without changing the composition of the water. Therefore, the pH stability

test is also a test of water composition changes during induced pH variation. Others suggest that pH is well buffered by the activity of aqueous carbonate, bicarbonate, and the carbonate minerals that are present. If so, relatively small changes in pH of groundwater should be observed when water of different pH or different composition is added to the system. For example, the pH of the groundwater should remain relatively constant when the pH of recharge water is lower than that of the groundwater, when radionuclides are included in the system, or after continued contact between the host rock and the groundwater because bicarbonate or carbonate react to maintain pH. Stability of pH is the measure of how much bicarbonate or carbonate is present to react with the infiltrating water. Changes in pH will be observed as the bicarbonate, carbonate, or other buffering constituent are consumed.

The pH stability of saturated-zone water can be estimated from previously published information, but estimating the pH stability of unsaturated-zone water will require more effort to isolate the different processes that control pH. Research detailed in other YMP studies will be important to this part of Test 1.

Changes in pH resulting from different chemical conditions imposed on the test apparatus will be initially modeled with the EQ3/6 code and other codes, if appropriate, such as MINTEQ and PHREEQE. Initial models will suggest possible reactions and processes controlling pH and water composition. The results of imposing pH conditions on water pH and composition will be measured by experiments with rock columns and crushed tuff obtained from Yucca Mountain. A discrepancy between measured and calculated results will require resolution and reexamination of calculations and measurements before information on pH stability and buffering capacity can be incorporated into the conceptual model. Agreement between measured and calculated results will indicate that the processes controlling pH stability were identified. Sets of hypotheses concerning processes and reactions that control pH and water

composition will be formulated as conceptual models and passed to Activity 8.3.1.3.1.1.2.

Test 2: Controls of Eh in saturated and unsaturated zones. Performance Assessment Issues 1.1 and 1.8 require information about the redox conditions at Yucca Mountain. Because radionuclide solubility depends partly on the oxidation state of the dissolving species, information about the control of the oxidation potential in groundwater is important for calculating the release of radionuclides to the accessible environment. Oxidizing conditions (high Eh) can result in increased mobilization of radionuclides; therefore, more transport of aqueous radionuclides would be expected at high Eh values. Also, aluminosilicates and oxides are generally more stable at a high Eh, therefore, active radionuclide absorbers are expected to be present in the system in oxidizing conditions.

As in the pH stability test above, water composition will change as the imposed Eh varies, and the composition changes will be measured. Changes in pH as a result of variation of Eh will also be measured so that the combined effects of Eh on pH and composition can be considered. Carefully controlled conditions will provide the opportunity for the necessary measurements. The processes controlling the reactions will be identified and passed on to the mathematical model.

This test will suggest how reactions with minerals and geochemical processes influence groundwater Eh and will show changes in Eh as a result of fluctuations in the alteration environment or in the composition of infiltrating water, such as increased acidity or the introduction of radionuclides. Initially, groundwater composition will be assumed to reflect a well-poised, oxidizing system, buffered by the available atmospheric oxygen. This condition will be evaluated during Test 2. Oxygen buffering with depth at Yucca Mountain will use literature values as well as measurements made during the unsaturated-zone hydrochemistry study (Study 8.3.1.2.3.2). Redox potentials will be calculated with different computer codes and various

minerals, and the composition of groundwater will be shown as a result of oxidation potentials controlled by oxygen partial pressure with depth or by different minerals. Redox potentials will also be measured by the concentrations of different ions of redox couples when possible. For example, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio relates to specific redox conditions, and the ratio can be measured spectrophotometrically by complexation with 1,10 o-phenanthroline. Gas chromatography methods for H_2 and O_2 measurement could be used to discern the redox conditions in Yucca Mountain groundwater. The amount of H_2 in oxidizing waters is expected to be low and may limit the practicality of the gas chromatograph method, however. Measurement of dissolved oxygen, redox-specific ion concentrations, and gas chromatography of dissolved gases are preferred to using Eh measurements made with standard platinum electrodes, that is, system Eh.

It is expected that different minerals and partial pressures of oxygen will determine the redox conditions at Yucca Mountain. The system may not be well controlled or “poised,” that is, a small change in composition, such as a change in hydrogen partial pressure, could result in a large (> 100 mV) change in redox conditions that may be of long or short duration. Lindsay (1979) illustrates the magnitude of the change in redox conditions when different minerals poise a system with different hydrogen and oxygen partial pressures.

Kinetics of mineral transformations will also be important in understanding the redox conditions at Yucca Mountain. For example, fracture coatings of manganese and iron indicate that oxidizing conditions prevail in some portions of the saturated and unsaturated zones.

Experiments with rock columns and with crushed material will be conducted to measure the redox conditions of water moving through these materials. Tests using water with high and low hydrogen partial pressure to control initial redox conditions will also be conducted so that the response of the material of interest can be understood. Discrep-

ancies between calculated and measured values will require greater attention before the Eh information can be used in the refined conceptual model.

Test 3: Tests to isolate water-rock (mineral) interactions. The water-rock-interaction tests are designed to evaluate compositional, pH, and Eh data obtained during the pH-stability test and redox-conditions test with regard to water-rock interactions that control pH, Eh, and composition. The minerals that could control the composition of saturated-zone groundwater have been discussed in several reports, and saturated-zone water compositions appear to be controlled initially by glass dissolution and then by aqueous silica activity. Reaction-path calculations compare favorably with mineralogical/petrological data and suggest that the major geochemical processes controlling saturated-zone water composition have been identified. The results of previous work on saturated-zone water composition will be incorporated into the preliminary conceptual model of groundwater chemistry, and interpretations of previous data will be reexamined as needed and used in the refined conceptual model. Data on stable isotopes of carbon, oxygen, and hydrogen will be included in the tests to further constrain the possible set of hypotheses that will result from the above tests. The isotope data will be supplied through Study 8.3.1.2.3.2 and related activities.

Few data on water composition from the unsaturated zone at Yucca Mountain have been reported. Yang et al. (1988) reported on water compositions extracted from unsaturated-zone material by triaxial compression. Benson (1976) reported similar data but from Rainier Mesa. Although more data will be made available from Study 8.3.1.2.2.7 (Hydrochemical Characterization of the Unsaturated Zone), Activity 8.3.1.2.2.4.8 (Hydrochemistry Tests in the Exploratory Shaft Facility), and Study 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry), the preliminary conceptual models will depend on computer simulations of water compositions in the unsaturated zone.

Yang et al. (1988) showed that the water content in material from the unsaturated zone at Yucca Mountain varied from 1 to 35 per cent by weight at matric potentials of -0.55 to -0.1 MPa, respectively. This report also included the composition of water extracted from the unsaturated-zone material. Others reported on the mineralogy of the rock matrix and fractures of different units at Yucca Mountain. Data on water content and composition will be combined with the data on matrix and fracture mineralogy, and possible compositions of water from the unsaturated zone will be calculated. The EQ3/6 code will be used to investigate water-rock interactions that include but are not limited to 1) reactions between water and rocks along specific flow paths that may occur only on minerals surfaces and not the entire mineral matrix at Yucca Mountain, 2) rock-water interactions with respect to equilibrium with a metastable solid phase, such as cristobalite or smectite clays, 3) rock-water interactions, and 4) strict thermodynamic equilibrium with stable minerals, such as quartz.

Integrate test data and hypotheses: generating conceptual models

Ideas about control of groundwater composition proposed in preliminary hypotheses will be integrated with test results, calculations, and data. This integration implies significant data analysis and reduction and will lead to the development of sets of hypotheses about the processes and reactions that control groundwater pH, Eh, and composition. The ideas from the preliminary hypotheses and the information from the tests and analyses will be integrated with the parameters and processes most influencing groundwater composition, and will provide the opportunity to refine the conceptual models. Alternative conceptual models will be proposed and will comprise different sets of hypotheses. The product of this activity will be a set of conceptual models of groundwater chemistry at Yucca Mountain that will show the parameters and processes important to groundwater composition and will be the basis from which a mathematical model can be developed. The proposed conceptual models, or sets of hypotheses about con-

trolling processes and reactions, will be the basis from which the mathematical models will be developed in Activity 8.3.1.3.1.1.2.

Develop mathematical models of Yucca Mountain groundwater

The goal of the groundwater chemistry model study is to develop a mathematical model of groundwater chemistry that can be used to predict the water composition as a result of various potential environments at Yucca Mountain. The potential environments include but are not limited to the changes in the current conditions resulting from construction of a nuclear repository, long-term heating of the rock surrounding a repository, and climatic conditions such as cooler, wetter climates at Yucca Mountain. Activity 8.3.1.3.1.1.2 is designed to use the hypotheses generated from laboratory tests, preliminary mathematical modeling, and field tests and refine them into a set of mathematical models of Yucca Mountain groundwater. Testing the models using laboratory data, natural analogs of processes that occur at Yucca Mountain, and sensitivity analysis will provide data needed to either accept a given model or to refine it to improve its predictive capability.

In Activity 8.3.1.3.1.1.2, the validity of the modeling approach will be tested. Mathematical models will be used to predict the results of experiments or known processes. Successful prediction of processes that are well-characterized will lend strength to the particular models chosen to model the processes in question. Uncertainty and sensitivity analyses will be conducted on the models so that the error (precision) and the accuracy of the predictions can be established.

Specific groundwater chemistry models will be tested in Activity 8.3.1.3.1.1.2. The models developed from the hypotheses in Activity 8.3.1.3.1.1.1 will be models of specific processes and models that combine smaller models of processes. The models will be tested to determine if they can predict the results of known experiments and test cases. Successfully tested models will be used to

refine the concepts about the processes and reactions that determine the pH, Eh, and composition of Yucca Mountain groundwaters. Models that are not successfully tested will be reconsidered and either refined or discarded. The groundwater chemistry model will be shaped during the course of model testing.

Finally, the mathematical models will be used to predict the effects of long-term water-rock interactions on water chemistry. Based on processes occurring presently or that are expected to occur during the lifetime of a repository, the predictions of groundwater pH, Eh, and composition as a result of continued mineral alteration will be made. Several sets of potential conditions will be imposed upon the calculations, including but not limited to extended heating into the far field, control of silica activity by precipitation of opal C-T and amorphous silica phases, and added recharge from a wetter climate. The uncertainties associated with such predictions will also be calculated so that other investigators know the degree to which the model can be believed. The last phase of the mathematical model activity will show the usefulness of the model for prediction and will also be ready for use as a tool to predict the effects of a given change on Yucca Mountain.

Regulatory rationale and justification

Several performance-assessment issues require information on groundwater chemistry to resolve the issues specified in *Code of Federal Regulations*, 10 CFR 60 (NRC 1983). This section describes the role of the study in support of resolution of Issue 1.1 (Total System Performance), Issue 1.5 (Performance of the Engineered Barrier System), and Issue 1.8 (Siting Criteria).

Issue 1.1. Total system performance for limiting release of radionuclides to the accessible environment

Support from Study 8.3.1.3.1.1 is required for the resolution of Issue 1.1 through Information Need 1.1.1 (Site Information Needed to Calculate Radionuclide Release to the Accessible Environ-

ment) and Information Need 1.1.4 (Determination of Radionuclide Release to the Accessible Environment in Association with Realization of Potentially Significant Release Scenario Classes).

Scenario classes of importance to Issue 1.1 and relevant to Study 8.3.1.3.1.1 are detailed elsewhere. Information from Study 8.3.1.3.1.1 will be used to evaluate parameters that relate to expected partial performance measures (EPPM) associated with different categories of scenario classes. Category E of the scenario classes is considered the nominal case and indicates no significant change in any natural barriers at Yucca Mountain. The parameters required for the nominal case and relevant to the groundwater chemistry study are the profiles of chemical constituents, including pH, Eh, and major and minor cations and anions. The current confidence in these parameters is low, but Study 8.3.1.3.1.1 will provide the required medium confidence level as defined in Issue 1.1. The parameters will be evaluated from data and calculations for both the unsaturated and saturated zones and will reflect the groundwater compositions, assuming no changes in the Yucca Mountain system occur.

Other performance parameters for Issue 1.1 required by Study 8.3.1.3.1.1 include support of the calculations of the radionuclide retardation factor (R_d) in both unsaturated and saturated zones. Relevant information, such as water compositions, will be supplied to SCP Investigation 8.3.1.3.7 (Radionuclide Retardation by All Processes) for calculating radionuclide retardation and for resolving Issue 1.1. The EPPM for radionuclide release through water pathways is required to be at a high confidence level.

Categories C and D are also of interest to Study 8.3.1.3.1.1. Category C includes partial failure of the unsaturated-zone barriers because of increased flow of water through the unsaturated zone, a rise of the water table into the unsaturated zone, or greater release of radionuclides into the saturated zone from the unsaturated zone as a result of alteration of the geologic material. Category D involves partial failure of the saturated-zone barriers

because of the emergence of new discharge points within 5 km of the candidate repository or an increased flow rate through the saturated zone.

Pathways for radionuclide release important to this study are releases via water movement through the unsaturated zone (Category C) and the saturated zone (Category D). As in Category E, the parameters of interest are chemical composition, pH, and Eh for both categories. In addition, parameters in both categories will include mineralogy, groundwater flow rates, and the geochemical processes controlling water composition, including sorption and mineral alteration. Category C will be concerned with increased infiltration into Yucca Mountain and the associated changes in water composition and mineralogy that could occur. Increased infiltration could be caused by increased irrigation in the recharge area or increased precipitation. However, the primary concern for Study 8.3.1.3.1.1 and for the resolution of Issue 1.1 is the overall effect on groundwater composition. The effects of changes in groundwater composition will be used by Investigation 8.3.1.3.7 to calculate the release of radionuclides to the accessible environment under the conditions of increased infiltration. EPPMs for radionuclide release via water pathways for Category C are required at a high confidence level for both increased infiltration and radionuclide release resulting from changes in geologic materials of the unsaturated zone. A medium confidence level is required for a water table rise into the unsaturated zone. Category D will be concerned with radionuclide release resulting from new water discharge points within 5 km of the candidate repository. The groundwater composition to higher flow velocity through the saturated zone will be suggested. This information will be important in calculating the radionuclide release to the accessible environment required by Investigation 8.3.1.3.7 and in resolving Issue 1.1. The EPPM associated with new discharge points is required at a medium confidence level, whereas the EPPM for radionuclide release resulting from an increased flow rate through the saturated zone is required at a high confidence level.

Information Need 1.1.1 requires information on parameters important to site performance. As discussed above, parameters important to site performance from the groundwater chemistry study are the major ion compositions, pH, and Eh. Information on these parameters will be collected and used with different environmental scenarios to estimate changes in groundwater composition over time.

Issue 1.5. Engineered-barrier system performance

Some information necessary to resolve this issue will come from Study 8.3.1.3.1.1 through Information Need 1.5.3 (Scenarios and Models Needed to Predict Radionuclide Release for Waste Package and Engineered Barrier Performance). This issue requires that information on changes in groundwater composition with time under different scenarios be incorporated into calculations of radionuclide release. In addition, Information Need 1.5.3 includes activities and subactivities that call for development of a database for geochemical modeling. Study 8.3.1.3.1.1 will contribute to the database through tests and analyses results.

Water quality information required in Information Need 1.5.3 will be evaluated so that different ranges of water compositions can be bounded for calculations of engineered-barrier system (EBS) and waste-package performance. Specific bounds on the water compositions will be established by the EBS and waste-package tasks. Supplemental information on groundwater composition and change in groundwater composition from concentrations of radionuclides will be provided.

Issue 1.8. Siting criteria-favorable and potentially adverse conditions

Issue 1.8 requires demonstration that the candidate repository site will contain radioactive waste for 10,000 to 100,000 years at the release limits stipulated in 10 CFR 60. This issue will evaluate several favorable conditions for radionuclide isolation and potentially adverse conditions that could compromise potential repository performance. Information on groundwater chemistry is required to evaluate the effects of different conditions on site per-

formance. Two favorable conditions and four potentially adverse conditions require information from Study 8.3.1.3.1.1.

Favorable conditions include groundwater chemistry that promotes precipitation and sorption of radionuclides; inhibits the formation of radionuclide particulates, colloids, and organic complexes; and inhibits transport of radionuclides. Study 8.3.1.3.1.1 will determine if these conditions exist and how stable they are over time and under different chemical environments.

Another favorable condition concerns the stability of the mineral assemblages at Yucca Mountain and the consequences of mineral weathering with time. Alteration of the present minerals into minerals with decreased radionuclide retardation capacity is undesirable, whereas it is considered favorable for the present minerals to change into those with increased ability to retard migration of radionuclides. Study 8.3.1.3.1.1 will evaluate mineral alteration and the resulting groundwater composition over time.

The first potentially adverse condition to be evaluated through this study is to determine any constituents or intensive parameters of the present groundwater chemistry that could increase the solubility of the materials comprising the EBS. These conditions include pH, Eh, and compositions of water that could cause increased chemical alteration of the EBS, thus altering or destroying its capacity to retard migration of radionuclides. The result of such alteration could be the potential for transport of larger amounts of radionuclides and ultimately release to the accessible environment in excess of the limits set by 10 CFR 60.

A second potentially adverse condition involves circumstances that could reduce the sorption of radionuclides, degrade the rocks and minerals that are important to sorption of radionuclides, or change the geologic system so that radionuclides released to the accessible environment could increase over time. Groundwater compositions,

under different scenarios, will play important roles in the evaluation of these potentially adverse conditions. Other information for this evaluation will come from studies in the geochemistry program on mineralogical/petrological mineral alteration and on mineral-transformation kinetics.

The third potentially adverse condition to be evaluated by this study is the possibility for maintaining a reducing environment in the hydrologic flow system. The stability of the groundwater chemistry with respect to redox and specific redox levels will be important for radionuclide transport calculations because most radionuclides tend to be least soluble under reducing conditions. The effects of groundwater compositions on radionuclide solubility under different Eh and environmental conditions will be evaluated. Information from Investigations 8.3.1.3.4 (Radionuclide Retardation by Sorption Process) and 8.3.1.3.5 (Radionuclide Retardation by Precipitation Process) will be used to assess this potentially adverse condition.

The fourth potentially adverse condition is the effect of surface impoundments on the transport of radionuclides to the accessible environment. This condition implies increased infiltration of water into the rocks and minerals of Yucca Mountain, a higher water table in locations near the impoundments, or increased mineral alteration in the unsaturated zones because of alteration of groundwater composition in the unsaturated and saturated zones as a result of increased infiltration that induces changes in minerals and rocks. The effects of greater infiltration on groundwater composition and mineral alteration will be calculated, and the effects of changing groundwater compositions on radionuclide release will be estimated by this study and calculated through Investigation 8.3.1.3.7 (Radionuclide Retardation by All Processes).

Rationale for Tests

Technical rationale and justification

Role of study in groundwater chemistry model

The goal of this study is to provide a groundwater

chemistry model by developing conceptual models (Activity 8.3.1.3.1.1.1) and mathematical models (Activity 8.3.1.3.1.1.2). Initially, different preliminary conceptual models will be evaluated because several sets of parameters, geochemical processes, and chemical environments could affect groundwater composition. Considering the different aspects of the preliminary models separately is the most efficient way to examine the possibilities and to determine those factors important to the development of the groundwater chemistry model. The tests and analyses will show how different chemical parameters will be identified and isolated. Testing and calculations will suggest the importance of parameters, such as pH and Eh, and will isolate the variables that determine them. Each test is designed to consider a specific parameter and different variables that could be important to groundwater composition. The product of the planned tests and analyses will be the integration of the test and calculation results into the preliminary models. The product of Activity 8.3.1.3.1.1.1 will be a set of relevant conceptual models used qualitatively to show different relationships between important parameters and groundwater chemistry. The conceptual model will be used in Activity 8.3.1.3.1.1.2 as initial input for the development of the mathematical model. The conceptual models will concentrate initially on both fracture flow and matrix flow. Data for one flow mechanism or the other can be disregarded should only one flow mechanism be deemed important to radionuclide transport.

Relationship to other site characterization activities

The unsaturated zone at Yucca Mountain could provide both a barrier and a pathway for radionuclide migration from the proposed nuclear repository. The release of radionuclides from a repository must be compatible with regulatory limits. Performance Assessment Issue 1.1 will evaluate the rate of radionuclide release to the accessible environment. To resolve the regulatory issues, a database on groundwater chemistry is required that includes data on the rock-water interactions controlling such parameters as pH, Eh, and the ionic

composition of groundwater.

The geochemical processes proposed using preliminary models cannot be developed satisfactorily without additional information on the parameters of interest. This information, which will come from other studies as well as this one, will include data on mineralogy and petrology, mineral alteration, mineral-transformation kinetics, sorption of radionuclides and other constituents, climates in effect in the past, and data concerning composition of existing saturated and unsaturated-zone water. These studies will provide information on the kind, abundance, and spatial variability of minerals (SCP Study 8.3.1.3.2.1), possible reactions to which the minerals could be subjected (Study 8.3.1.3.3.2), the amount of radionuclides and other constituents that could adsorb onto different minerals (Investigations 8.3.1.3.4 to 8.3.1.3.6), the composition of groundwater of Yucca Mountain and vicinity (Study 8.3.1.2.2.3), the composition of water derived from the unsaturated zone (Study 8.3.1.2.2.7), and past climates in the Yucca Mountain area (Study 8.3.1.5.1.2 and other studies in Investigation 8.3.1.5.1). Information derived from this study will more fully demonstrate the interaction between groundwater and rocks or minerals at Yucca Mountain through a series of tests, described below. The data from this and other studies will make possible a more specific description of water chemistry along potential flow paths and of the possible groundwater composition that could result from changes in chemical environments.

Some data exist on the interactions of rocks and groundwater, showing that these interactions can cause significant changes in groundwater composition and mineralogy. Few studies, however, show the specific effects of rock-water interactions on parameters such as pH because the tests are difficult to perform and the parameters are related to several geochemical processes.

The chemical composition of water is modified as it flows through different parts of Yucca Mountain. Water moving through the unsaturated zone is pos-

sibly in contact with minerals much longer than water moving through the saturated zone. The effects of long contact time on groundwater composition are continued dissolution of host rocks and possible precipitation of secondary minerals within relatively small rock volumes. The concentration of dissolved constituents in unsaturated-zone water is expected to be high because the volume of water is reduced by evaporation of water into the air in the unsaturated-zone pore space or by the decrease in the H_2O activity through hydration of different minerals. Data from Study 8.3.1.2.2.3 (Characterization of Percolation in the Unsaturated Zone—Surface-Based Study) and rate of evaporation or mineral hydration will be used to suggest conditions that could result in water with high concentration of dissolved constituents in the unsaturated zone.

Rock-water interactions appear to be a more continuous process in the saturated zone than in the unsaturated zone. Rock-water interactions in the saturated zone may even approach a steady state in geologic time. Periodic wetting and drying in the unsaturated zone, however, may slow mineral alteration significantly or result in the formation of greatly different secondary minerals than those found in the saturated zone. Thus, more mineral alteration is expected in the saturated zone and possibly more secondary mineral precipitation, owing to increased dissolution of host minerals. Study 8.3.1.2.3.2 (Characterization of Saturated Zone Hydrochemistry) will provide additional data on groundwater composition, and Investigation 8.3.1.3.2 (Mineralogy, Petrology, and Rock Chemistry) will provide the mineralogy of new bore holes. This information will be used in modeling different reactions with minerals and water and in refining the conceptual model developed by this study so that a realistic idea of groundwater composition can be formulated.

Study 8.3.1.3.1.1 (Groundwater Chemistry Model) will use information from the unsaturated zone, saturated zone, and other studies mentioned above. The activity demonstrates interactions between rocks and water that control groundwater composi-

tions. Computer codes employing calculations from thermodynamic databases will be used with the water data and data from other studies to show plausible reactions and reaction paths that could produce the observed groundwater composition. Tests will also be used to supply more detail on the variables that determine different parameters. The reactions suggested as a result of groundwater-composition data and computer calculations will be refined, as needed, to show more specifically the role of Yucca Mountain rocks and minerals in the control of groundwater composition and to suggest how different chemical environments change groundwater composition through time.

Existing data on groundwater chemistry will be integrated into the groundwater chemistry model, and different preliminary models of groundwater chemistry will be proposed. The preliminary models will be the starting point for further refinement of ideas and will provide a list of data needs so that a more realistic conceptual model can be developed. Consideration of alternate preliminary models will result in a conceptual model that examines different factors controlling groundwater chemistry. Elimination of preliminary models that are not supported by the data will result in a set of thorough conceptual models that will be fundamental to the development of more quantitative mathematical models.

The tests outlined above are proposed for three reasons. First, these tests will be used to evaluate different aspects of each preliminary model so that the model's validity can be tested in parts. The test results will indicate the importance of different parameters and also the relevance of the different models to the overall objective of this study. Those preliminary models remaining after testing will be considered further.

Second, the test results will provide substantial data for this study, other studies, and for activities in the geochemistry and hydrology investigations. The database created will be used in Activity 8.3.1.3.1.1.2. Other tasks, such as Investigation

8.3.1.3.5 (Radionuclide Retardation by Precipitation Process), require information on groundwater chemistry to be included in the database. The information obtained from these tests is required for the development of the final conceptual model and the mathematical model in Activity 8.3.1.3.1.1.2. This database will be a continuing resource for other studies, activities, and tasks concerned with the chemical modeling of Yucca Mountain.

Third, the proposed tests will examine the preliminary models and will guide the refinement of preliminary models and formulation of the conceptual models. This process will make it possible to critically evaluate the preliminary models through test results and to eliminate or reduce the inadequacies of different preliminary models. Through this method, those aspects of the preliminary models that are not relevant to the goals of this study will be identified and eliminated while the most important elements to groundwater composition are being studied further.

This method for developing conceptual models was chosen so that different preliminary models could be proposed initially, tested thoroughly, and a final model developed that illustrates the groundwater chemistry at Yucca Mountain. The method also allows for the inclusion and testing of different models, as discussed in the SCP Overview 8.3.1.1 (Role of Alternative Conceptual Models). Each preliminary model consists of a set of hypotheses about the Yucca Mountain system, and the tests above prove or disprove them. This method of development also consolidates data on groundwater chemistry presently found in diverse sources and other studies within the YMP, thereby helping the development of the mathematical model and providing a valuable database for other studies and activities.

Tests 1 and 2 are designed to provide information concerning the processes and reactions that control composition, pH, and Eh of groundwater at Yucca Mountain. Knowledge of the rock-water interac-

tions controlling the concentrations of different groundwater constituents is central to understanding both the present groundwater chemistry and the groundwater composition that could result from rock-water interactions under different chemical conditions over time. Changes in one of the parameters of interest in Tests 1 and 2 will also change the values of the other parameters of interest. Thus, the relationship between the different parameters, such as pH, redox conditions, and different minerals that control or determine groundwater composition, can be examined in detail. The tests may also indicate that some of the parameters are stable over wide ranges of chemical environments, and the impact of these changes on the final conceptual model is minimal. Also, transport of radionuclides through Yucca Mountain in water depends upon groundwater composition, and solubility of radionuclides may be affected by pH, redox, and the minerals present. Understanding the role of each parameter on radionuclide solubility will lead to development of a more representative conceptual model that qualitatively predicts the possible fate of radionuclides in groundwater at Yucca Mountain over time. This type of qualitative prediction will be useful to other studies, especially Investigation 8.3.1.3.7 (Radionuclide Retardation by All Processes).

Development of the mathematical models in Activity 8.3.1.3.1.1.2 will integrate the different tests and hypotheses from Activity 8.3.1.3.1.1.1. Tests in the first activity will provide the information required to derive the conceptual models of groundwater chemistry, and the models will be tested and quantified in the second activity. Sensitivity and uncertainty analyses will be part of the testing-phase mathematical models and will provide necessary information about how reliable predictions of groundwater chemistry can be. Activity 8.3.1.3.1.1.2 will provide the groundwater chemistry model that is required in the SCP.

The duration of tests will be approximately one year, or long enough to show no significant water composition changes over several weeks, that is,

“steady-state” conditions. Calculation of the effects of changes in different parameters on water composition, however, will take considerably less time because no laboratory tests are involved. The rock-column experiments, especially those with unsaturated-zone material and unsaturated flow conditions, will take the most time because of the complex test apparatus and slow flow rates anticipated. Replication of rock-column experiments will be limited because of the duration of each experiment. However, replication of computer calculations will be done frequently because they take much less time.

The tests will provide a more detailed understanding of the parameters and geochemical processes controlling groundwater composition. The test results will provide data on and initial estimates of groundwater composition for development of the mathematical model in Activity 8.3.1.3.1.1.2.

The tests were designed in kind and number to examine initial preliminary models and refine them into specific conceptual models to guide further work on groundwater chemistry at Yucca Mountain. Integration of test results and preliminary conceptual models will yield a final conceptual model providing information on groundwater composition both at present and in the future, as changed by the influence of different environments.

Test constraints

The tests described here will have little impact on the repository site. Samples for rock-column experiments will be obtained from available drill cores through the sample-management facility (SMF). Data on mineralogy and petrology will be obtained on the samples, as needed, to ensure that well-characterized material is used in the tests.

The accuracy and precision of the analytical methods used in these tests will not limit the use of test results. Analyses of pH and soluble constituents are relatively simple, and the detection limits are low enough to provide useful information on the parameters of interest. Calculation of Eh using

concentration ratios of redox couples such as $\text{H}_2/\text{H}_2\text{O}$, $\text{Fe}^{3+}/\text{Fe}^{2+}$, or $\text{Mn}^{4+}/\text{Mn}^{2+}$ depend on the analyses of the redox couples. Gas chromatography analysis of $\text{H}_2(\text{g})$ and spectrophotometric determination of $\text{Fe}^{3+}/\text{Fe}^{2+}$ should not place undue constraints on the Eh values calculated. The procedures and the limits on precision and accuracy of different measurements made from these tests will be developed to reflect sound scientific practice. The accuracy of numerical values will be checked against National Institute of Standards and Technology (NIST) standards, and precision of measurements will be determined by obtaining values from multiple samples, when possible. If an estimate of the precision of a measurement from a given test cannot be made owing to the duration of a given test, this estimate will be made in a different medium. For example, replicate samples for measuring the pH of water moving through a rock column cannot be obtained, but the stability of pH measurements from a sample can be demonstrated by determining the pH of known standards or simulated water compositions. Also, care will be taken during experiments that do not permit replication so that the best measurements of different parameters are made.

Errors that propagate through computer calculations will be estimated with statistical methods to assess sensitivity to errors in input data. Errors enter into the calculations by uncertainty in the analytical values and error in the values that constitute the database used by the chemical speciation codes. Because large uncertainty can result from error in database values, the sensitivity of the database used will be ascertained. The sensitivity analysis will be more fully developed in the later stages of Activity 8.3.1.3.1.1.1 and in Activity 8.3.1.3.1.1.2 as the mathematical model is developed, but initial estimates of model stability will be worked out in the former activity.

The main limitation of these tests is the amount of time needed to complete them. It is conceivable that data could be collected from rock-column experiments for several years, but that time frame

is longer than the scope of this study. Therefore, the time needed to establish the experimental conditions (for example, the attainment of unsaturated flow or steady-state flow in a column) will be minimized so that data collection can begin as soon as possible at the start of the experiment. The length of these tests and the complexity of the experimental apparatus will also limit the number of replications that can be completed. Replicate samples will be run to check the repeatability of the tests when flow rates through the materials of interest are rapid. When test apparatus is limited, or if column supports are limited, tests of different materials will be given preference over replicate runs of the same material. Because of the few replications planned in these tests, the experiments will be established in the most rigorous manner to minimize error in measured values.

These tests will be done remotely, so they will not interfere with other tests or with the ESF design and construction. Repository conditions will not be simulated because this study is concerned with far-field effects, not those of the proposed repository and its accessible environment. The results from this study are also to be used in modeling and interpreting the experiments in Study 8.3.1.3.6.1, Dynamic Transport Column Experiments.

C. DISSOLVED SPECIES CONCENTRATION LIMITS AND COLLOID BEHAVIOR

Purpose and Objectives of Studies

This study plan describes two of the studies included in Investigation 8.3.1.3.5, Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment. These studies are required by the Site Characterization Plan (DOE 1988) before licensing and construction of a proposed repository for high-level radioactive waste at Yucca Mountain, Nevada. The purpose of these studies, Dissolved Species Concentration Limits (Study 8.3.1.3.5.1) and Colloid Behavior (Study 8.3.1.3.5.2), is to supply data for calculating radionuclide transport along potential transport pathways from the repository to the accessible environment. These calculations are needed to address the overall system-performance objective for radionuclide releases in 10 CFR 60.112 (NRC 1988) (Issue 1.1, Total System Performance, SCP Section 8.3.5.13), to make findings on the postclosure system guidelines and the technical guidelines for geochemistry in 10 CFR 960.3-1-5 (DOE 1988) (Issue 1.9, Higher-Level Findings—Postclosure, SCP Section 8.3.5.18), and to address the siting criteria of 10 CFR 60.122 (Issue 1.8, NRC Siting Criteria, SCP Section 8.3.5.17). Specifically, Issue 1.1 requires estimates of the means and standard deviations of the solubility limits of radionuclide-bearing compounds under the water-chemistry conditions expected at the site.

Water moving through the emplacement area toward the accessible environment can transport radionuclides in two ways: either as dissolved species in the water or as particulate material (that is, natural colloidal materials or radiocolloids) carried by the water. This investigation will supply data and models that can be used to calculate the concentration limits of dissolved radionuclides in local water at the Yucca Mountain site. These concentration limits will be used directly by performance-assessment models of radionuclide trans-

port. This investigation will also supply data and models that describe the formation and stability of radiocolloids in local water. This information will be used in assessing the likelihood of colloid transport (Investigation 8.3.1.3.7, Radionuclide Retardation by All Processes). The information will also be used in the calculations for Issue 1.1, Total System Performance. Radionuclide solubility and speciation data and models will also be used to support modeling of sorptive behavior as a function of water chemistry and radionuclide chemistry (Investigation 8.3.1.3.4, Radionuclide Retardation by Sorption Processes).

It is not practical to measure the solubilities of all radionuclides that may exist in radioactive waste under all conditions that may occur at the repository or along flowpaths to the accessible environment. Therefore, the technical approach used to select radionuclides for solubility measurements and to select the conditions of these measurements is based on three criteria:

- radionuclides present in quantities that are large in comparison with Environmental Protection Agency (EPA) release limits;
- radionuclides that are likely to reach solubility limits during transport based on current knowledge of radionuclide chemistry and expected repository conditions; and
- conditions for solubility experiments that will bound expected conditions at the repository or along flow paths to the accessible environment.

The radionuclides of primary concern are discussed in SCP Section 4.1.3.1.1, Key Radionuclides. A review of the chemistry of important radionuclides is also given in SCP Section 4.1.3.4, Processes Affecting Radionuclide Concentrations and Speciation in Solution. These sections, along with descriptions of the expected groundwater chemistry (SCP Section 4.1.2, Ground Water Chemistry) and changes in water chemistry resulting from waste emplacement (SCP Section 4.2, Geochemical Effects of Waste Emplacement), form the basis for the selection of the solubility experiments discussed below. The initial emphasis is on

solubility and speciation for americium, plutonium, and neptunium. Measurements are also planned for uranium, thorium, radium, zirconium, tin, and nickel. The latter elements are included in the testing program so that the concentrations can be used as upper bounds for transport assessments.

Investigation 8.3.1.3.5, Radionuclide Retardation by Precipitation Processes, consists of two distinct studies. The goal of the first, Study 8.3.1.3.5.1, Dissolved Species Concentration Limits, is to comply with the NRC's position paper (NRC 1984) by providing solubility data (concentration limits) for dissolved species of important radionuclides under conditions that are characteristic of the repository and along flow paths to the accessible environment, and to provide a predictive capability for solubility under conditions for which solubility has not been empirically determined. The results of this study will be used in the assessment of radionuclide releases to the accessible environment and to assess the existence of favorable or potentially adverse conditions at the site.

Study 8.3.1.3.5.1, Dissolved Species Concentration Limits, will consist of three separate Activities: Solubility Measurements (8.3.1.3.5.1.1), Speciation Measurements (8.3.1.3.5.1.2), and Solubility Modeling (8.3.1.3.5.1.3). The objective of the solubility-measurements activity is first to measure the solubilities of important radionuclides under closely controlled experimental conditions. The objective of the speciation-measurements activity is to identify important aqueous species of radionuclides and to determine their formation constants under prescribed conditions. The formation constants (sometimes referred to by the more generic term of equilibrium constants) define the equilibria that exist between the radionuclide and its complexes in solution. This activity will be necessary when data are unavailable from sources outside the Yucca Mountain Project (YMP) or when verification of the validity of available data is required. This activity will be conducted concurrently with Activity 8.3.1.3.5.1.1, Solubility Measurements, and is intended to fill any data gaps so that a com-

plete body of solubility data can be adequately tested by thermodynamic modeling. The objective of Activity 8.3.1.3.5.1.3, Solubility Modeling, is to implement the thermodynamic models and determine the data needed to calculate radionuclide solubilities over the entire range of conditions expected at the repository site. It is clear that there is a significant interdependence of all three activities in this study and that all are vital for the success of the study.

The second study, Study 8.3.1.3.5.2, Colloid Behavior, will focus on understanding the behavior of radiocolloids. Within the context of this study plan, radiocolloids are defined as colloidal aggregates composed of radionuclides or simple complexes of radionuclides. These should be distinguished from complex colloids that are composed of clay or other particulate matter onto which radionuclides are sorbed. Complex colloids are considered in detail in Study 8.3.1.3.4.1 (Batch Sorption) under Activity 8.3.1.3.4.1.4 (Sorption on Particulates and Colloids). The transport properties of these complex colloids are also considered in Study 8.3.1.3.6.1 (Dynamic Transport) under Activity 8.3.1.3.6.1.5 (Filtration). The interface to these Studies is discussed below. The goal of this study is to determine the stability of radiocolloids under site-specific conditions at the repository or along flow paths to the accessible environment. The results will be used in the assessment of radionuclide releases to the accessible environment and to assess the existence of favorable or potentially adverse conditions at the site. This study plan considers only one activity in the Colloid Behavior study: Colloid Formation, Characterization, and Stability (Activity 8.3.1.3.5.2.1). The objective of this activity is to determine the conditions that are favorable to the formation and stabilization of the radiocolloids and to characterize the physical and chemical properties of these colloids. The information obtained in this activity will be used specifically by Issue 1.1 (Total System Performance) and Investigations 8.3.1.3.4 (Radionuclide Retardation by Sorption Processes) and 8.3.1.3.6 (Radionuclide Retardation by Dispersive, Diffusive, and Advective

tive Transport Processes). Colloid Modeling (Activity 8.3.1.3.5.2.2) will be included under the domain of the Solubility Modeling Activity (8.3.1.3.5.1.3).

In selecting these experiments, we have also considered the generic NRC technical position entitled “Determination of Radionuclide Solubility in Ground Water for Assessment of High-Level Waste Isolation” (NRC 1984). This technical position serves as guidance in the preparation of detailed plans for experiments to determine radionuclide solubility and requires that if radionuclide solubility is used as a factor in limiting radionuclide release, experiments must be designed to determine solubility under site-specific conditions. The experiments discussed in this study plan are meant to satisfy the requirements of the technical position.

The various parameters that influence solubility can be divided into three groups:

- those parameters that define the conditions controlling solubility (water chemistry, temperature, and radiation field),
- those parameters that define radionuclide behavior (radionuclide chemistry, colloid behavior, and kinetic data), and
- those parameters necessary to understand precipitation processes (models).

The primary areas of choice in designing solubility experiments involve the conditions of the experiment and the elements chosen. Five specific parameters have been considered in designing the experiments for the solubility studies: 1) water composition, including pH and Eh (speciation of redox-sensitive radionuclides), 2) temperature, 3) identity of the solid that controls solubility, 4) the presence of other solids, and 5) radiation effects, such as radiolysis. Solubilities that represent upper limits on radionuclide concentrations are of primary concern in defining the experiments. However, solubility data alone, without an understanding of the basic thermodynamic processes that determine the solubilities are of limited value. Thus, our approach is intended to stress an understanding

through speciation determinations. Thermodynamic modeling will also be used to help understand the solubility and speciation behavior of the radionuclides in the multicomponent aqueous systems found in the Yucca Mountain environment.

An important part of this investigation is modeling the solubility and speciation of radionuclides (SCP Section 4.1.3.4, Processes Affecting Waste Element Concentration in Solution). Modeling will be used for two purposes: 1) to assess the importance of the various parameters that influence solubility and speciation (for example, water composition) and 2) to calculate solubilities under conditions not directly covered by the solubility experiments. Existing models of solubility and speciation of radionuclides are based primarily on equilibrium methods. This emphasis will continue. Equilibrium models require thermodynamic data for solids that are likely to precipitate and for aqueous species that may be present in the water. We are deriving these data from literature sources, from other sources within the Yucca Mountain Project (for example, SCP Section 8.3.5.10.3.2), and from the solubility and speciation data collected as part of this investigation. Nonequilibrium or kinetic models will be used as needed to describe certain aspects of radionuclide solubility.

Movement of natural radiocolloids is a transport mechanism that may be active under conditions at the Yucca Mountain site that may limit the effectiveness of the sorption barrier in retarding migration. To assess the potential for colloid transport (Investigation 8.3.1.3.4, Radionuclide Retardation by All Processes), information is needed about the likelihood of colloid formation under extant water chemistry conditions at the Yucca Mountain site and the stability of colloids once formed. Two radionuclides that may form stable colloids under these conditions have been identified: plutonium and americium (SCP Section 4.1.3.4). Because these radionuclides also contribute significantly to the radioactivity of the waste inventory, we plan to examine their potential for colloid formation and to perform stability experiments.

Rationale for Species Concentration Limits and Colloid Behavior Studies

Rationale for dissolved-species concentration limits

We will determine the solubilities of certain radionuclides in the far-field environment. The radionuclides studied will be those found in the waste to be emplaced at Yucca Mountain. Certain experiments will be conducted in samples of groundwater obtained at the Yucca Mountain site. The results will be used to determine whether the site is suitable for disposal of radioactive waste. First, we will measure the upper limit of concentrations of the various ionic and colloidal radionuclides. These data alone will not be sufficient because groundwater conditions (such as temperature, Eh, and pH) may change; therefore, we will also determine the actual species present and the equilibrium quotients of the various reactions. In this manner, thermodynamic data will be obtained that can be used in solubility modeling to calculate solubility limits under any possible conditions at the repository site, including both the near and far field. This approach includes an assessment of the solubility limits of colloidal radionuclides. The rationale and justification for each of these tasks are outlined in more detail in the sections below.

Rationale for radionuclide solubility measurements (Activity 8.3.1.3.5.1.1)

Radionuclide concentrations in water passing through the emplacement area can be limited by two mechanisms: low dissolution rates of the solid waste form or solubilities of individual radionuclides. If solid-waste dissolution rates are low enough, it may not be necessary to depend on solubilities to limit radionuclide concentrations. However, the solid waste forms have not yet been determined, and therefore the dissolution rates of the solid waste are unknown. (Note, however, that information on the water chemistry at the potential emplacement horizon in the near field will be determined in Study 8.3.4.2.4.1, Rock-Water Interactions at Elevated Temperatures.) Determination of radionuclide solubility provides an upper

bound on radionuclide concentrations in solution and provides a basis for extrapolation to long-term behavior. These concentration limits may be higher than those obtained from solid-waste dissolution rates for many important radionuclides. Only if the rate of groundwater flow through the waste is sufficiently slow to permit saturation of the water with radionuclides will the solution concentrations approach the solubility limits. Therefore, an assessment of radionuclide release rates using a saturation-limited dissolution model represents the most conservative approach possible.

As radionuclides are transported from the emplacement area to the far field along flow paths to the accessible environment, changing water chemistry (pH, Eh, oxidation state, and concentrations of complexing species) due to degradation of either the engineered-barrier system or the geological barrier can alter solubilities. A knowledge of radionuclide solubilities under the conditions along possible flow paths is necessary to assess this scenario. Investigation 8.3.1.3.1, Water Chemistry Within the Potential Emplacement Horizon and along Potential Flow Paths, provides information on flow path conditions.

Long times are frequently required to reach steady-state conditions for radionuclide solubility/dissolution. For this reason every conceivable solubility determination cannot be investigated. We will select radionuclides, groundwater, pH, Eh, and temperature to bracket the expected range of conditions by choosing parameters that represent lower and upper limits.

Radionuclides. The radionuclides selected will be limited to nuclides with solubility-limited dissolution rates (sparingly soluble). Americium, neptunium, plutonium, thorium, uranium, radium, nickel, tin, and zirconium will be investigated in this study. Cesium, technetium, strontium, iodine, and carbon have such large solubilities (determined from the literature database) under the conditions expected at Yucca Mountain that their dissolution rates are limited by the dissolution rate of the

waste, and therefore, these nuclides will not be considered in this activity.

Water compositions and temperatures. Ideally, water samples with compositions that bracket the range of waters expected in the vicinity of Yucca Mountain should be chosen for solubility and speciation measurements. Much of the needed information concerning the water composition in the unsaturated zone will come from Study 8.3.1.2.2.7 (Unsaturated Zone Hydrochemistry). The present strategy calls for the use of two waters that are currently available from the saturated zones at the site for the initial solubility experiments. Then, as information on the water composition in the unsaturated zone becomes available, it will be compared with the composition data for the two saturated waters. If the water compositions are sufficiently disparate to lead to probable significant differences in solubilities (that is, higher levels that would potentially jeopardize solubility as a barrier to migration), then synthetic unsaturated-zone waters will be prepared and used for additional solubility determinations. Note that the variation in solubility based on changes in water composition will be tested to the extent possible with existing thermodynamic data to determine if additional solubility determinations with synthetic unsaturated-zone water are warranted. In this way, it should be possible to avoid an excessively large suite of experimental determinations.

For the initial solubility experiments, the two waters available from the site are Well J-13 water and Well UE-25 p#1 water. Well J-13 water taps the Topopah Spring Member tuff, which contains the repository horizon. Thus, this water was initially expected to be representative of the water composition of the unsaturated zone near the proposed emplacement area. However, preliminary results indicate that unsaturated-zone water has approximately three times greater ionic strength than Well J-13 water. Well UE-25 p#1 taps the carbonate aquifer that underlies the emplacement horizon. This water has an ionic strength and total carbonate content higher by approximately an

order of magnitude than Well J-13 water. Well UE-25 p#1 water represents natural water with the highest concentrations of dissolved species expected in the vicinity of Yucca Mountain. The water from both wells is oxidizing. Generally, radionuclide solubility studies under oxidizing conditions lead to higher solubilities for a number of radionuclides than would occur under mildly or strongly reducing conditions. Thus, these tests will provide conservative results. Note also that preliminary data on the unsaturated-zone waters place the dissolved-species concentration between that of Well J-13 and Well UE-25 p#1. Thus, the choice of these two waters for the initial experiments appears reasonable based on preliminary data.

In addition, solubility measurements will be done in dilute sodium-perchlorate electrolyte. These measurements will provide data for 1) a relatively simple system in which only hydrolysis occurs and only oxides or hydroxide precipitates are being formed and 2) scenarios in which dilute waters re-enter the repository after the thermal period.

The perchlorate electrolyte is used because the perchlorate anion, ClO_4^- , is a hard base with low tendency to coordinate, though some cases have been established in which a small complexation between perchlorate ions and metal ions occurs. However, these interactions are the exception rather than the rule. This fact is demonstrated by the many reported studies for the actinide hydrolysis reaction that are carried out in perchlorate medium with concentrations ranging from very dilute (~ 0.1 M) to concentrated (~ 5 M).

An additional variable in the groundwater composition is the possible presence of dissolved species derived from the waste package and other engineered-barrier components. Tests on the reactions of Well J-13 water with the host rock and on the metals from which the waste container may be fabricated (SCP Section 8.3.5.9.2, Information Need 1.4.2, Material Properties of the Container) were initiated as part of the waste-package task of the YMP. Only small changes in water composition

associated with the contact of Well J-13 water with the metals tested have been found. However, small changes in critical constituents (for example, redox-buffering agents) can significantly impact solubilities. If changes in the concentrations of critical components are observed in the experiments to determine waste-package dissolution properties, the solubility conditions outlined in this study must be re-evaluated and changed as necessary. Here, too, an attempt will be made to predict the change in solubilities of radionuclides as a result of the changes in water composition using existing thermodynamic data before experimental solubility determinations are initiated so that the number of empirical determinations can be kept to an acceptable level.

The maximum temperature of the host rock in which liquid water is present is expected to be limited by the boiling point of water at Yucca Mountain (95°C). The solubility experiments that use Well J-13 water will be conducted at temperatures between 25 and 90°C. This span covers the range from pre-emplacement temperatures to the maximum temperature at which solubility would be important. For Well UE-25 p#1 water, solubility tests will be limited to a maximum temperature of 60°C. Maximum temperatures in the saturated zone under the emplacement area and those along flow paths away from the emplacement area are expected to be less than 60°C (Johnstone et al. 1984).

Constraints on solubility studies. The solubility of radionuclides in solutions of near-neutral pH and relatively low carbonate concentration (total carbonate from 0 to about 0.1 M) is generally controlled by solids containing hydroxides or carbonates. The formation of hydroxide and carbonate solids depends on the activity, $a(\text{H}^+)$, of the hydrogen ion in solution; therefore, accurate solubility measurements require continuous control of $a(\text{H}^+)$. The conventional measure of $a(\text{H}^+)$ is pH. Strictly, pH is defined operationally to yield a quantity that is easily and reproducibly measured and approximately equally to $-\log a(\text{H}^+)$. For solutions of low ionic strength and with pH values

in the range for 2 to 12, the operational definition is within 0.02 units of $-\log a(\text{H}^+)$. For the purpose of solubility determinations, standard deviations in pH of 0.2 of a unit should be satisfactory for these near-neutral solutions. If the solubility tests show a stronger pH dependence, the pH will be controlled more tightly, if possible.

The accuracy of measured pH values is controlled by 1) the accuracy of the standard buffer solutions, certified by the National Institute of Standards and Technology (NIST), that are used to standardize the pH electrodes, and 2) the degradation of the pH electrodes in the time between calibrations. The accuracy of a newly restandardized pH electrode will be set by valid standard buffer solutions, which should not exceed 0.01 of a pH unit. However, pH electrodes degrade when they are continuously in contact with the solution. Semiweekly restandardization will limit the resulting degradations to between 0.05 of a pH unit at 25°C and 0.1 at 90°C.

The solution concentrations of the radionuclides are determined by radionuclide counting (alpha, beta, and gamma counting) of solution aliquots. Determination of concentrations requires accurate measurement of volume and counting rates. Volumes are measured with calibrated digital pipettes and Class-A volumetric pipettes and glassware having tolerances better than 1.5%. Given sufficient counting time, counting rates can be measured to very high precisions. Their accuracy is limited by the accuracy of commercially available NIST-certified standard sources (typically 2 to 3%). These combined accuracies lead to an accuracy of about 5% for the concentration determination.

Radionuclide counting will be done to a precision of 5% whenever possible within reasonable counting times. For trace-level concentrations relatively long counting times may be required to reach this level of precision, and sample counting to a lower precision may become necessary. Table 37 lists counting times in minutes of a 1 ml sample of ^{237}Np , ^{239}Pu , and ^{243}Am that are necessary to

reach 5%, 20%, and 50% precision at 10^{-10} , 10^{-9} , and 10^{-8} M, respectively. If the solubility tests indicate that a higher precision than the initially chosen one is needed to refine solubility limits, the sample will be recounted over a longer time.

Rationale for the study of radionuclide speciation (Activity 8.3.1.3.5.1.2)

The study of speciation of radionuclides is fundamentally important to the determination of radionuclide solubility in the groundwater at Yucca Mountain. Speciation is strictly defined as 1) the identification of the radionuclide, 2) the determination of its oxidation state, and 3) the formula or structure of the ionic or solid complex—that is, the stoichiometry of the ion as complexed by OH^- ions (for example, hydrolysis) or by other ligands (for example, carbonate, fluoride, phosphate). Speciation can be determined to a lesser degree by, for example, deducing only the oxidation state of the radionuclide in question.

Although direct solubility measurements (Activity 8.3.1.3.5.1.1) will provide limits for the concentrations of important radionuclides under certain specific groundwater conditions, they cannot possibly

provide concentration limits for all foreseeable groundwater conditions. Therefore, a basic thermodynamic characterization of radionuclide speciation is needed to bridge any gaps in the data acquired from direct solubility determinations and to provide the fundamental thermodynamic constants needed for modeling solubility under conditions that are not specifically considered in the solubility determination. In the speciation study, we will attempt to identify the important complexes of the radionuclides (for example, oxidation states, the formula or structure of the ionic or solid complex, and the extent of hydration or complexation) that are likely to form under the prevailing groundwater conditions (such as temperature, pH, Eh, and the concentration of complexing agents) at the Nevada Test Site (NTS). The speciation study will also attempt to determine the formation constants for these complexes.

Rationale for approach to speciation activity.

Carbonate ions are a principal potential complexing agent in the groundwater at the NTS, which has carbonate-ion concentrations as high as 3×10^{-3} M. Actinides, which typically have quite low solubilities in near-neutral solutions, can be complexed by

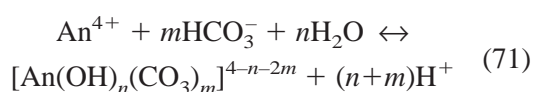
Table 37. Precision as a Function of Counting Time and Solution Concentration*

Radionuclide	Precision	Counting time needed to achieve precision (mins)**		
		10^{-10} M	10^{-9} M	10^{-8} M
^{237}Np	5%	43,127	4,313	431
	20%	2,695	270	27
	50%	431	43	5
^{239}Pu	5%	486	47	5
	20%	31	3	1
	50%	5	1	$\ll 1$
^{243}Am	5%	149	15	2
	20%	10	1	$\ll 1$
	50%	1	$\ll 1$	$\ll 1$

*1 ml sample, 100% counting efficiency. ** 2σ values.

carbonate ligands to form species that have increased solubility limits. For this reason, the speciation study will focus on the carbonate complexes of the important radionuclides. If Activity 8.3.1.3.5.1.1 (Solubility Measurements) and Activity 8.3.1.3.5.1.3 (Solubility Modeling) identify other important complexing agents, such as fluoride, phosphate, and humates, speciation studies for these other agents will be considered.

Carbonate-ion speciation of the actinides under solution conditions such as those expected in the far field involves equilibria such as



where An refers to an actinide element.

It is difficult to study these equilibria directly using conventional methods because, at environmentally relevant pH values, the concentration of An^{4+} is extremely low. These experimental difficulties can be overcome in several ways. We are currently pursuing two of the more promising approaches. First, we have developed modern, ultrasensitive, laser-based spectroscopic techniques that include the absorption-based probes known as photoacoustic spectroscopy (PAS), the related method of photothermal-deflection spectroscopy (PDS), and the complementary, emission-based probe known as laser-induced fluorescence (LIF) spectroscopy. Because of the extreme sensitivity of these methods, speciation data can be obtained directly for solutions having site-specific characteristics. The second approach is the method of competitive complexation that uses conventional (transmission-based) electronic-absorption spectroscopy to obtain speciation data. For some radionuclides, such as plutonium and americium, this approach requires some deviations from the actual solution conditions and compositions expected for the groundwater at the repository site so that sufficiently high concentrations of the radionuclide species can be maintained. However, for the more soluble radionuclides, such as uranium and neptunium, this

method is directly applicable under site-specific conditions in many cases. The principal advantage of this method is experimental expediency in that the spectroscopic techniques are well established and straightforward in implementation. Therefore, scoping experiments can be carried out with minimal expenditure of resources. In addition, this method will provide valuable spectral signatures for speciation at higher concentrations, which can be used to assist in interpretation of speciation data obtained from other methods.

Both the methods based on advanced laser-spectroscopic probes (PAS, PDS, and LIF) and the competitive-complexation method rely on information contained in the electronic absorption-band structure of the radionuclide species to characterize speciation. The principal electronic transitions that give rise to these characteristic absorption bands are Laporte-forbidden $f-f$ transitions. Although these transitions do not involve bonding electrons, the energies, intensities, and numbers of transitions in the total absorption spectrum change in a very sensitive way in response to perturbations induced by the coordination environment (that is, the ligand field) of the radionuclide ion. Thus, different species of the same metal ion possess distinctive absorption spectra. However, because the spectral transitions are, in general, parity-forbidden, the intensities are extremely low ($\epsilon < 50 \text{ M}^{-1} \text{ cm}^{-1}$ is not uncommon). This fact, coupled with the inherent low solubility of these species under solution conditions in the groundwater, is the cause of the formidable experimental challenge to the characterization of speciation in these systems.

The principal advantage of the methods based on advanced laser-based spectroscopic probes lies in the extreme sensitivity of the detection schemes. In general, photothermal effects occur when light is absorbed by any state of matter (solid, liquid, or gas) and the absorbed energy is subsequently converted into heat as a result of radiationless deactivation. The evolved heat produces two prominent effects. One is a thermal expansion that creates an acoustic pressure wave, which is the effect used in

PAS. The second is the generation of a gradient in the index of refraction in the medium surrounding the absorber. This gradient can be probed optically and is the basis of PDS. Photoacoustic and photothermal-deflection spectroscopies result when these two effects are engendered by monochromatic light tuned through a wavelength range of interest. The acoustic signal is detected using a very sensitive pressure-transducing device, such as a piezoelectric crystal. The index-of-refraction gradient is determined by precisely measuring the deflection of the light beam from a small probe laser. Thus, the only difference between PAS and PDS is in the method of detection of the evolved heat. In both cases, the magnitude of the measured signal as a function of excitation wavelength is directly related to the absorption spectrum of the illuminated sample. The extreme sensitivity of these two techniques results when a high-intensity, short-duration, pulsed laser is used to excite the samples and the analytical signal is measured using gated detection methods. Laser-induced fluorescence spectroscopy is simply analytical fluorimetry that uses the special properties of pulsed-laser excitation to gain sensitivity and resolution. It can be seen that PAS, PDS, and LIF are exactly complementary techniques. If a sample loses the energy of excitation by emitting light, there is little thermal effect, and LIF is the appropriate tool for analysis. Conversely, if the excitation energy is readily lost as heat, little light is emitted, and PAS and PDS are the best methods.

PAS and PDS offer the same advantage for enhanced sensitivity relative to conventional transmission-based absorption spectroscopic probes as do LIF and other emission-based spectroscopic probes. This advantage is that both PAS and PDS are true zero-background analytical tools; that is, the analytical signal is measured against a negligible background signal. This method contrasts with conventional absorption methods in which the analytical signal is derived from the small difference between two large light levels. In addition, laser-excited PAS and PDS (and LIF) are particularly effective for analytes with narrow absorption tran-

sitions because the absorption bands can be scanned using a single laser dye. Accordingly, these techniques are ideally suited for the study of actinide speciation because the electronic spectra for these species are dominated by the characteristically narrow $f-f$ transitions.

Photoacoustic and photothermal-deflection spectroscopies and LIF have what may legitimately be called ultimate sensitivity. It has been demonstrated that LIF can detect as few as eight molecules of a substance in solution. However, most of these measurements (excluding vibrational PAS and PDS) involve probing electronic spectroscopic transitions and, as such, are notoriously difficult to relate a priori to specific structural (speciation) features. The spectra are quite sensitive to structure, but the relationships between spectral signatures and structures must generally be established empirically. Accordingly, part of our task will be to establish these spectral signatures for the actinide species extant under environmentally relevant conditions. We will use existing and new analytical data that have been derived from using competitive complexation and other methods (see below) to establish spectral signatures for radionuclides that exist at higher concentrations than those expected in the natural environment. Using PAS and PDS, we will perform serial dilution studies ranging from high concentrations to those of environmental significance. This approach will enable us to track the evolution of speciation down to environmentally significant conditions or the detection limits of the techniques. Implicit in all this work is the necessity of modeling the spectral properties of complex mixtures of species to assist in assigning spectral signatures and in assessing the contributions of each species to the total spectroscopic signal.

For the studies based on the competitive-complexation method, the citrate ion has been chosen as the competitive-complexing agent. Previous work with the actinides has shown that the carbonate ion competes successfully with the citrate ion for the coordination sites on the actinide ions. The competitive-complexation method involves three stages of

investigation: 1) the study of the pure carbonate systems, 2) the study of the pure citrate systems, and 3) the study of the mixed carbonate-citrate systems. All three stages are necessary so that the formation constants for the carbonate complexes can be expressed in terms of the principal radionuclide species present in aqueous solutions (An^{4+} in Eqn. 71). Some results for the pure carbonate and citrate complexations of the actinides already exist in the literature. The present study will confirm and extend the previous work for the first two stages.

This approach to the determination of the identity of the radionuclide species and their formation constants often necessitates some deviation from site-specific conditions at the repository. In particular, the concentrations of the radionuclides, such as plutonium and americium in the test solutions, will have to be significantly higher than those likely to be present in the groundwater because of the relative insensitivity of conventional electronic-absorption spectroscopy. To permit a reliable determination of the speciation and thermodynamic constants, the concentrations of the various species must be large enough to provide easily measurable absorbance values. However, by determining thermodynamic data, the behavior of the radionuclides can, in principle, be extrapolated to any regime. These studies will also provide species-specific spectral signature data for use in interpreting results obtained by other methods.

Two valuable adjuncts to the laser-spectroscopic and competitive-complexation methods described above are x-ray absorption spectroscopy (XAS) and nuclear-magnetic-resonance (NMR) spectroscopy. These techniques enable the direct determination of structural information (coordination numbers, ligand identities, bond distances, and valence) for species in solution, allowing, in principle, for a complete unambiguous specification of speciation. The conventional XAS technique is applicable at the millimolar concentration level for the actinides, and advanced detection methods can likely extend this range down to the micromolar level. Likewise, 1H , ^{13}C , and ^{17}O NMR techniques are readily

applicable at the millimolar level for radionuclides and can be extended to lower levels by using more powerful magnetic fields. These lower detection limits are still not sufficiently sensitive for directly probing many of the actinide species that exist under environmentally relevant conditions. However, the combination of competitive-complexation methods (high concentrations), XAS and NMR methods (high and intermediate concentrations), and PAS, PDS, and LIF methods (intermediate and low concentrations) should provide a complete description of radionuclide speciation.

Other experimental methods of studying radionuclide speciation are also available, including potentiometric-electromotive-force (EMF) determinations as a function of complexant concentration and pH, solvent extraction, ion exchange chromatography, solubility, and enthalpy titrations. None of these methods is without certain limitations and drawbacks. Nonetheless, all are potentially useful for this speciation study, and a continuing appraisal of the progress made with the competitive-complexation method and PAS, PDS, and LIF methods vis-a-vis the possibility of applying these other methods seems most prudent at present.

As described below, many of the detailed tests and analyses that make up this speciation study are under development. As this activity evolves, we will change the methods and approaches as necessary to obtain the information needed in the most practical manner. At present, we expect to conduct all of the proposed experiments (with the exception of x-ray absorption spectroscopy) at Los Alamos National Laboratory. In addition, it is expected that site-specific data on the speciation of the radionuclides of interest can be obtained through simulation of anticipated repository conditions. Therefore, this activity should have no direct impact on the proposed Yucca Mountain site, with the exception of the potential need for groundwater samples from the site. Although the expected results from this activity are needed by several other activities and information needs (see "Purpose and Objective of Studies" above), the results

are not needed for the initiation of any other YMP activity. Thus, there are no specific time constraints on this activity. The required level of accuracy, where meaningful and appropriate, and the precision for most of the measurements in this activity are conservatively estimated at $\sim 5\%$. At this level, the data will be valid and significant to the issues and information needs. In all cases, we will endeavor to obtain results with the highest possible levels of statistical significance.

Constraints on the speciation activity. It is impractical to study speciation for all of the radionuclides that may be present in the waste to be emplaced at the repository. For this reason, the primary guidance for choosing which radionuclides to study will come from the EPA listing on release limits in 40 CFR 191 (EPA 1982, Appendix A, Table 1). Potential candidates for speciation studies will be those radionuclides that are expected to be present in the repository in quantities that are large in comparison with their EPA release limits. The potential list of radionuclides will be further constrained to include only those that are likely, based on present knowledge of radionuclide chemistry and expected repository conditions, to have groundwater concentrations that are limited by solubility during transport. Additional guidance in selecting candidate radionuclides for speciation studies will come from Activities 8.3.1.3.5.1.1, Solubility Measurements, and 8.3.1.3.5.1.3, Solubility Modeling. The initial emphasis for the speciation studies, based on the above criteria, will be on neptunium, plutonium, and americium. Subsequent studies will be conducted as necessary for uranium, thorium, radium, zirconium, tin, and nickel. Note that the speciation and complexation properties of many of the radionuclides in this second tier are already fairly well understood because there are stable nuclides (zirconium, tin, and nickel) that can easily be handled, or because the radionuclides have low specific activities (thorium and uranium) that greatly simplify handling. Thus, additional speciation studies for this second tier should be limited in scope and are presently scheduled for the final two years of the Speciation task. Speciation determinations for

all radionuclides enumerated above can be conducted using the suite of techniques described above.

It is also impractical to carry out speciation studies under all conditions that may occur at the repository and along all flow paths to the accessible environment. For this reason, experimental conditions for the speciation studies (concentration of radionuclides, temperature, pH, Eh, and concentration of complexing agents) will be chosen (in consultation with investigators in Study 8.3.1.2.2.7, Unsaturated Zone Hydrochemistry) to provide the soundest possible thermodynamic results, which, in some cases, may require that data be collected under conditions that are not typical of those expected at the repository site. However, reliable thermodynamic results will also allow extrapolation with minimal uncertainty of radionuclide solubilities and other properties to site-specific conditions.

Rationale for solubility modeling studies (Activity 8.3.1.3.5.1.3)

Solubility modeling analysis has two purposes: 1) to assess the importance of the various parameters that influence the solubility and speciation of radionuclides (for example, groundwater chemistry) and 2) to calculate the solubilities of radionuclides under conditions that are not directly covered by Solubility Measurements (Activity 8.3.1.3.5.1.1) and Speciation Measurement (Activity 8.3.1.3.5.1.2).

The primary environmental parameters that control solubility and speciation are groundwater chemistry, groundwater temperature, and radiation. The ranges of these parameters that will be covered in this analysis are governed by the conditions expected at the proposed Yucca Mountain repository and along flow paths to the accessible environment.

The conditions covered by the solubility modeling analysis are the same as those outlined by Kerrisk for solubility measurements. Table 38 summarizes these conditions. The sensitivity of the solubility of important radionuclides to variations in groundwater chemistry and temperatures within the

ranges listed in Table 38 will be evaluated. If it is experimentally determined that radiation is a significant parameter, attempts will be made to evaluate the sensitivity to variation in the radiation field. Input will also be obtained from Study 8.3.1.3.1.1, Groundwater Chemistry Model, to insure that all potential groundwater chemistries are considered in modeling radionuclide speciation.

Rationale and justification for the approach used to model solubility. The initial approach to modeling solubility and speciation is to use an equilibrium (thermodynamic) model. The model chosen is the EQ3/6 chemical-equilibrium computer program. Modeling solubility and speciation involves a two-step process: 1) validating the model and the thermodynamic data that support the model by comparing calculated solubilities and aqueous species concentrations of radionuclides with results from well-controlled experiments and 2) using the validated model to calculate solubilities as needed for sensitivity analyses or for support of performance assessment.

Using EQ3/6 to calculate radionuclide solubilities requires a set of thermodynamic data for the major aqueous species and the solids that could precipitate for each radionuclide of interest, as well as data for the constituents of the groundwater at Yucca Mountain. These data are obtained by ana-

lyzing the results of speciation and solubility experiments involving the radionuclides, by performing theoretical calculations, and by making comparisons with elements whose chemical behavior is similar. Many of the data needed have been obtained from the chemical literature. An evaluation of this literature database, modification of existing data, and the addition of new data found to be needed to model solubility represent a major part of this modeling activity. A significant amount of database evaluation and modification has taken place under the auspices of the Geochemical Modeling and Database Development Activity (WBS 1.2.1.4.5) at Lawrence Livermore National Laboratory. However, this work has not emphasized radionuclides.

It is not certain at this time whether equilibrium models will describe the solubility of all important radionuclides. Models involving kinetic behavior or other nonequilibrium phenomena may be required to adequately model observed behavior. Nonequilibrium models will require additional input information, including rate constants and reaction mechanisms. It is improbable that all necessary input data can be collected under the experimental activities described here. If nonequilibrium modeling appears necessary, it will only be implemented using assumptions concerning missing input data, and conclusions drawn from the results

Table 38. Environmental Conditions for Solubility Modeling

Parameter	Range of conditions
Water chemistry	Simple neutral electrolyte (NaClO ₄) through complex, multi-ion solution approximating Well UE-25 p#1 water.
pH	5 to 11
Temperature	20 to 95°C
Redox conditions	0 to 500 mV (versus normal hydrogen electrode)
Radiation	Alpha activity from waste-element isotopes. The effect of radiation is actually incorporated into the pH/Eh ranges.*

*Kerrisk (1985)

of the nonequilibrium modeling will be qualified with respect to the level of approximation and the projected impact of the approximate result.

In addition to solubility, speciation, and thermodynamic data obtained from the literature and other sources within the Yucca Mountain Project (SCP Section 8.3.5.10.3.2), solubilities of important radionuclides obtained from solubility measurements (Activity 8.3.1.3.5.1.1) and formation constants of important aqueous species obtained from speciation measurements (Activity 8.3.5.3.5.1.2) are needed to perform the analyses described here. Data are also needed that describe the expected conditions at the repository and along flow paths to the far field. The most important environmental information is groundwater chemistry (Activities 8.3.1.2.2.7.2, Aqueous-phase Chemical Investigations; 8.3.1.2.2.4.8, Hydrochemistry Tests in the Exploratory Shaft Facility; and 8.3.4.2.4.1.3, Composition of Vadose Water from the Waste Package Environment).

Constraints on the solubility modeling study.

Solubility modeling depends on site-characterization activities to define existing and expected future conditions at Yucca Mountain. Solubility calculations used in these models will be validated only for the range of environmental conditions covered by Solubility Measurements (Activity 8.3.1.3.5.1.1) and Speciation (8.3.1.3.5.1.2). Small extrapolations are possible for groundwater compositions or temperatures different from those from which the data have been derived. Equilibrium modeling is limited by the assumption that, over the time scale of interest, chemical equilibrium exists in the system. This limitation is relieved to some extent by the validation process. Solubility and speciation measurements will identify the solids controlling solubility. This experimental work, used in conjunction with assumed equilibrium in the aqueous phase, allows application of this technique.

The Solubility Modeling activity is presently scheduled to begin in fiscal year 1994. This start-

ing date anticipates the availability of a version of EQ3/6 that has undergone software quality-assurance review. This starting date will be timely enough to accomplish the necessary interfaces and provide the needed support for SCP Activities 8.3.1.3.5.1.1 and 8.3.1.3.5.1.2. However, if initiation of modeling studies is further postponed, or if the modeling code must be qualified, the schedule for Activity 8.3.1.3.5.1.2 in particular will need to be adjusted.

Rationale for the study of colloid formation, characterization, and stability (Activity 8.3.1.3.5.2.1)

Rationale and justification for the selection of properties of radiocolloids

Several radionuclides that are expected to be found in the waste emplaced in the potential repository are known to form natural colloids under chemical conditions similar to those found in the groundwater at the Yucca Mountain site. These colloids could form in the emplacement area or along flow paths to the accessible environment, and thus radionuclides could be transported as colloids or dissolved species, or both. In addition, the colloids may disintegrate into other soluble ionic species. Therefore, a thorough characterization of these colloids under relevant conditions is essential to permit assessment of the concentration limits and transport mechanisms for the radionuclides at the site. Substances other than radionuclides form small particles that can be suspended in solution. Radionuclides may be adsorbed on these solids, forming complex colloids that could be transported in groundwater. Complex colloids are considered in detail in Study 8.3.1.3.4.1 (Batch Sorption) under Activity 8.3.1.3.4.1.4 (Sorption on Particulates and Colloids). The transport properties of these complex colloids are also considered in Study 8.3.1.3.6.1 (Dynamic Transport) under Activity 8.3.1.3.6.1.5 (Filtration). This study will attempt to characterize the radiocolloids by collecting data and other existing information pertinent to the following questions.

- Which radionuclides can form colloids?

- What chemical and environmental conditions favor the formation of these colloids?
- What are the chemical and physical properties of these colloids?
- What factors influence the stability of these colloids?

The first question has been investigated in detail. At present, only plutonium and americium have been identified definitely as colloid-forming radionuclides. In the initial stages of the investigation, we will emphasize the study of plutonium colloids because it is expected to be an important form of plutonium in the far field. In subsequent stages of this study, we will focus on colloidal americium. If the solubility studies identify colloidal neptunium as an important species, this species will also be incorporated into the latter stages of the colloid study. No other colloidal radionuclides of consequence are anticipated.

The remaining three questions all pertain to the fundamental properties of the natural radiocolloids, but in a very broad sense. To focus this investigation, it is first necessary to enumerate the specific colloidal properties that will be studied and to indicate the importance of these properties to YMP issues and information needs. The emphasis of the research in this activity will be to elucidate these specific colloid properties. All fundamental colloid properties fall into one of two categories: those that can be classified as physical characteristics and those that can be classified as chemical characteristics. This distinction is convenient primarily for organizing the discussion of this activity.

The most important physical characteristics of the natural colloids are particle size, density, and bulk charge. All three of these are expected to be especially important in determining the transport characteristics of the natural colloids because these parameters govern such important properties as filtration, adsorption, and sedimentation. Knowledge of these physical characteristics is also crucial to

the investigation of the chemical properties of the colloids because the chemical interactions will be predominantly heterogeneous (that is, colloidal suspensions, or sols, interacting with species dissolved in solution). Thus, it will generally be desirable to be able to specify colloidal surface areas (which can be estimated from particle-size data) and bulk charges for experiments designed to elucidate the chemical properties of the colloids.

The most important chemical characteristics of the natural colloids are chemical reactivity and colloidal structure. Reactivity refers to the rates and mechanisms of all chemical processes (including self-radiolysis) affecting colloid formation and stability, as well as to chemical equilibria. Thus, both equilibrium (thermodynamic) and nonequilibrium (kinetic) conditions are important to this study. We will study chemical reactivity to determine the influence of solution conditions on colloid formation and stability. In particular, fundamental processes, such as the hydration of the aquated Pu^{4+} ion and the subsequent formation of Pu(IV) colloid or the dissolution of colloidal suspensions, are all manifestations of the thermodynamic or kinetic properties of the colloids. Colloidal structure refers to the specification of colloid stoichiometry, the description of chemical bonding at the molecular level, and a specification of the disposition of the various atoms in the colloidal matrix. There are several important reasons for characterizing the structure of colloids. One of these is to obtain chemical bonding data (for example, metal-to-oxygen bond strengths) to aid in interpreting observed reactivity data. Another is that a valid structural description of the disposition of the atoms in the colloid will aid in understanding and modeling colloid formation and dissolution and in understanding physical properties, such as bulk charge distributions and adsorptive interactions.

Rationale and justification for the tests and analyses selected to investigate the properties of radiocolloids

We are currently developing the various tests and analyses to be performed for this activity. Surpris-

ingly little is currently known about either the physical or the chemical characteristics of even the best-characterized radiocolloid, the Pu(IV) colloid. Thus, it is impossible to determine at this point which of several possible test methods will provide the best route to a desired piece of information. For this reason, no preference for any particular method has been established. Instead, a reasonable and prudent course of experimentation has been devised to provide data on all of the aforementioned colloidal properties. Certain procedures and techniques that will form the basis of the initial phase of this investigation are outlined below. However, as data are collected and analyzed, new experimental approaches and techniques for acquiring additional information necessary for thorough characterization of the colloids will be suggested. These new approaches will be incorporated in this activity, as necessary.

Before describing the specific test methods to be implemented in the initial phase of the investigation, several general remarks are in order. The first concerns the specification of the experimental conditions that will be used in this activity to characterize colloidal properties. Because so little is currently known about the properties and behavior of the radiocolloids and because the best experimental approaches have not yet been identified, we will not initially emphasize experimental conditions that duplicate those expected at the proposed repository. Rather, most of the initial work will be carried out under conditions (such as dilute mineral-acid solutions at room temperature) that have been used in earlier efforts to study actinide colloids, which is the most direct approach to assessing the various test methods. Subsequent experimental work in this study will be more project-specific and will be carried out under a wide range of experimental conditions, including variations in the chemical composition of the water, temperature, and intensity of the radiation field. This experimental range will bracket the actual range of conditions expected at the repository and along the flow paths to the accessible environment. However, for completeness, we will rigorously simulate

certain anticipated repository conditions (for example, by duplicating the chemical composition of water from Wells J-13 and UE-25 p#1 for part of the experimental work).

At this time, it is expected that all of the proposed experimental work will be carried out at Los Alamos National Laboratory and that site-specific data on colloid properties can be obtained by simulating anticipated repository conditions. Thus, this activity should have no direct impact on the proposed Yucca Mountain site, with the exception of a possible need for groundwater samples from the site. Although the results from this activity are needed by several other activities and information needs (see "Purpose and Objective of Studies" above), it is not necessary that the results be available for these activities to begin. For this reason, there are no specific time constraints on this activity. Finally, the required levels of accuracy, where meaningful and appropriate, and precision for most of the chemical and physical properties of the colloids are conservatively estimated at $\sim 5\%$. Many of these data will still be valid and significant to the issues and information needs at even lower levels of accuracy or precision. Despite this fact, we will endeavor to obtain results with the highest possible levels of statistical significance.

Rationale for the tests selected to elucidate the physical characteristics of radiocolloids. The physical characteristics of the radiocolloids to be investigated are particle size, particle density, and bulk particle charge. A logical working assumption in this investigation is that these physical properties may vary as a function of the chemical composition and temperature of the solutions in which the colloid forms and as a function of time. To assess the effects of these variations, we plan to conduct experiments in which pH, ionic strength, ionic composition, and temperature are varied. The investigation of the time dependence in the physical properties of the colloids is particularly important because the degree of time dependence will indicate the stability of the colloidal particles. Experiments will be conducted as a function of

time to 1) determine the rate of aggregation and disaggregation of the particle, 2) establish whether there are upper limits to particle size or density, and 3) determine whether these properties reach steady-state values. We will conduct the experiments with different isotopes, at least for the plutonium-colloid investigation, to examine the influence of alpha radiation fields on the physical properties of the colloids.

Particle-size determination of colloids. The initial efforts to determine colloid particle size will rely on a technique known as autocorrelated photon spectroscopy. This work will be done in collaboration with the Investigation 8.3.1.3.6, Radionuclide Retardation by Dispersive, Diffusive, and Advective Transport Processes. This method is based on the quasi-elastic scattering of incident laser light by particles suspended in solution and undergoing random diffusion (that is, Brownian motion). The scattered light is collected and analyzed for intensity as a function of time. The result is an autocorrelation function, which is deconvolved for the diffusivity of the colloid particle. From the diffusivity, we can calculate the hydrodynamic radius (that is, the particle size in solution) by the well-known Stokes-Einstein relationship. In addition, by studying the angular dependence of the scattered light intensity, it is possible to determine the degree of sphericity of the colloid particles. The degree of sphericity is not a high priority in this investigation, but some samples may be examined for this property.

This technique has many advantages over other possible particle-sizing methods, such as electron microscopy and ultrafiltration. Foremost among these advantages is that APS provides absolute size information on colloid particles suspended in the solution in their natural hydrated state. Further, the size information includes both the mean particle size and the distribution of particle sizes about the mean. It is also possible to detect bimodal size distributions and degrees of sphericity as discussed above. In contrast, electron microscopy can provide specific size information but requires that the

particles be dried. Thus, the data provided by this method may not adequately reflect colloid properties. Ultrafiltration using submicrometer-sized filters can be used on colloid samples suspended in solution, but the result is only upper and lower limits of particle size. The limits are set by the availability of commercial filters of sufficiently uniform pore size, and at present, this availability is inadequate. In addition, colloidal particles adsorbed on the filters can interfere with this filtration method.

APS is not easily applied if there is a high degree of polydispersity in the colloid particle size. In addition, extreme care must be taken to remove or exclude dust particles and gas bubbles from the test solutions. Based on some preliminary results, the former limitation is not expected to cause problems in the radiocolloid study, and the latter limitation can be overcome with attention to experimental technique. The accuracy of the APS method is expected to be $\sim 5\%$, which is adequate for this investigation. The level of precision is comparable and is also adequate for this study.

Determination of colloid particle density. We will determine the density of the radiocolloid particles by an ultracentrifugation technique. Solutions of the suspended colloid are centrifuged at very high centripetal force to effect a separation of the colloid, and the resulting stratified solution is analyzed for colloid concentration as a function of depth in the centrifuge tube. We can then calculate the colloid density from the laws of sedimentation. However, a critical component in this calculation is particle size. Thus, to determine the density, it will be necessary to determine the particle size. All other factors involved in the density calculation are either experimental constants or well-known physical constants. In principle, it is possible to get some information about the density-dependent distribution of colloids by analyzing sufficiently small depth increments in the centrifuge tube.

There are few, if any, other methods for determining colloid particle density. It may be possible to use simple pycnometric techniques to get some

indication of colloid density, but because this approach is certain to be cumbersome and likely to be inaccurate, it is not currently under consideration. The accuracy and precision of the ultracentrifugation method for determining colloid particle density will be comparable to that obtained in the published report (Rundberg et al. 1988). These levels of accuracy and precision are expected to be adequate for this investigation. Finally, although adsorption of colloid particles on the centrifuge tube walls may alter the results produced by the ultracentrifugation method, it should be possible to mitigate this problem by proper treatment of the walls of the tubes or by correcting for this effect in the calculations.

Determination of colloid bulk charge. No specific decisions regarding the methods for determining the bulk charge on the colloidal particles have yet been made, but two approaches are currently under consideration. The first approach is to use electrophoresis, in which the charged particles of interest are suspended in an appropriate support medium and a high electric potential is imposed across a pair of electrodes in the medium. The charged particles then migrate in response to the electric potential. The extent of migration of the particles as a function of the applied potential and time can be used to calculate the charge-to-mass ratio of the particles. Then, having determined the average mass of the colloid particles from size and density data, we will be able to ascertain the average bulk charge on the colloid particles. A commercial instrument (ZetaSizer) is available for these determinations.

A second possible approach to determining bulk charge on the colloids is to use the proven ability of certain simple inorganic anions, such as nitrate (NO_3^-), to precipitate the colloid as a “salt” of the anion. This method is used to study the variations in the concentration of the unprecipitated colloid as a function of the concentration of the simple anion. Mathematical expressions similar to solubility-product expressions are then used to determine the particle charge. Although this approach appears to

be straightforward from an experimental point of view, it is unclear at this time whether such a technique would be generally applicable to the study of all radiocolloids and under all the relevant chemical conditions.

It is impossible at present to assess the accuracy or precision of either of these techniques for determining bulk charge on the colloids. However, the most important piece of information concerning bulk charge is the sign of the charge (that is, cationic or anionic). This will be determined with high accuracy by either method. For the absolute magnitude of the charge, uncertainties of from 10 to 20% are probably acceptable. The anion-precipitation technique is inherently less accurate than the electrophoresis method because the data analysis required in the precipitation method involves construction of logarithmic concentration plots (“log-log” plots), which tend to be somewhat insensitive. However, even this assessment is tentative because it is still unclear what the magnitude of the bulk-charge values will be. Large values for the bulk charge would reduce the amount of uncertainty in the precipitation method. Clearly, the precipitation method offers the advantage of experimental simplicity. Thus, a definite choice of techniques for determining the bulk-charge parameter will likely have to await testing of both methods.

Rationale for the tests selected to elucidate the chemical characteristics of radiocolloids. The principal chemical characteristics of the radiocolloids to be addressed in this activity are reactivity and structure. It is expected that the chemical characteristics of the colloids will be influenced by the chemical composition and temperature of the solutions containing the colloids and will perhaps vary as a function of time. In fact, variation in the chemical composition and temperature of the solutions containing the colloids will be one of the primary methods used to elucidate the chemical reactivity properties of the colloids. The structure of the colloids may also be strongly dependent on the composition of the solutions, particularly with respect to the identities and concentrations of the

electrolytes. Thus, variations in solution pH, ionic strength, electrolyte composition, and temperature will be integral parts of this investigation. The effects of intense radiation fields may also strongly affect the chemical characteristics of the colloids, especially with respect to attainment of chemical equilibrium. Thus, investigations that use isotopes with differing specific activities are planned, at least in the case of the plutonium colloid.

Before we discuss specific tests, an important point should be emphasized: the approach to discerning the chemical properties of the radiocolloids differs distinctly from the approach to evaluating the physical characteristics of the colloids. The physical properties of the colloids are well-defined quantities that could, in principle, be investigated using a single technique with reasonable assurance that a specific value for the quantity of interest would result. For this reason, it is legitimate to compare the various techniques that could be used to solve a specific problem (for example, determining particle size by APS versus ultrafiltration) and to select the probable best technique. In contrast, although a host of possible techniques and procedures can be used to determine chemical properties (such as, colloid structure), the various methods provide complementary results, which, taken together, lead to a description of the chemical property of interest. For this reason, rather than focus on which of several methods is best for a particular characterization and why, we here describe all of the tests that are currently planned. The lists described are not exhaustive but will be supplemented as new techniques become available during this investigation.

Chemical reactivity of colloids. The study of colloid reactivity will be concerned primarily with elucidating the rates and mechanisms (that is, the kinetic properties) of colloid formation and dissolution under a variety of conditions, particularly those conditions expected at the proposed repository site. In addition, the possible existence of chemical equilibrium (that is, the thermodynamic properties) in the colloid systems will be explored.

The principal technique for these investigations will be ultraviolet, visible, and near-infrared electronic-absorption spectroscopy. Kinetic data will be acquired as a function of time. This technique is based on the measurement of the characteristic electronic transitions in species that are either suspended in solution (colloids) or dissolved in solution (reactants and dissolution products in the colloid formation and dissolution processes). Because every species possesses a characteristic electronic spectrum whose spectral-band intensities are proportional to the concentration of that species, it is possible, under optimum conditions, to use these electronic spectral data both to identify and quantify the various species present in the colloid containing solutions. The accuracy of this technique is typically quite good, even for weakly absorbing species at moderately high concentrations. For example, mineral-acid solutions of Pu(IV) can be detected routinely at 10^{-4} M with an accuracy of $\sim 5\%$. This level of accuracy is adequate to obtain meaningful kinetic-rate data and equilibrium constants. However, it may prove necessary to use even lower concentration levels in this study to properly simulate expected site-specific conditions. If this is the case, it is still possible to obtain these same electronic spectral data, but PAS or related methods would be necessary.

Another general approach to characterizing reactivity is to apply electrochemical methods to study the redox properties of the colloids. The principal emphases in these investigations will be to determine the potentials at which reduction and oxidation of the colloids take place and to investigate the kinetics of the redox transformations. These redox properties are of fundamental importance to colloid characterization because they are a viable mechanism for colloid degradation and radionuclide dissolution. These experiments will primarily use modern instrumental techniques, such as linear potential-sweep voltammetry, controlled-potential coulometry, and standard three-electrode electrochemical-cell designs. These designs will generally use either solid (platinum, gold, silver, carbon) or liquid (mercury) working electrodes. Using

these instrumental methods, we can vary the potential of the system in a continuous manner while confining the redox transformations to the immediate vicinity of the working electrode. Additional experiments are planned using homogeneous redox reagents, such as the Ce(IV)/Ce(III) redox couple, and heterogeneous reducing reagents, such as zinc amalgam. In this way, it will be possible to assess the differences in the redox reactivity of the colloids and to ascertain whether the reactivity is significant in the presence of dissolved redox reagents or surface-active redox reagents. The accuracy of the data to be collected in this activity is conservatively estimated to be 5 to 10 mV, which is entirely adequate. It is expected that the accuracy of any rate data collected in this study will be 5%, which is also quite adequate.

Structure of colloids. The emphasis in this activity will be on obtaining chemical-bonding information for the colloids and on attempting to specify the disposition of the atoms in the smallest repeating structural entity ("unit cell") of the colloids. An absolute specification of the stoichiometry of the colloids would also be extremely valuable, but such information is not obtainable using currently available techniques. Thus, stoichiometric information must come from inferences drawn from other structural data. The principal techniques to be used in this characterization are x-ray diffraction and Raman vibrational spectroscopy. Small-angle neutron scattering (SANS) has also been used recently to determine plutonium colloid structure and morphology. Los Alamos has a neutron-scattering facility at which such work can be performed. However, these are protracted experiments from the perspective of both data acquisition and data reduction and analysis, and the results can be ambiguous. Thus, our efforts will focus first on the more tractable x-ray-diffraction and vibrational-spectroscopy work to attempt to obtain the desired structural data. If SANS experiments are warranted following the initial efforts, they will be pursued.

We will use standard x-ray-diffraction methods

similar to those used to characterize the crystal symmetry and unit-cell parameters in powdered solid samples for both dried colloid samples and concentrated suspensions of the colloid in solution. If well-defined x-ray patterns are obtained, the spacings of the lines in the pattern will be used to calculate the simple structural parameters, such as unit-cell dimensions, according to well-established formulae. The application of x-ray-diffraction methods to concentrated, undried suspensions is by no means straightforward, but this technology has been successfully demonstrated in our laboratories. It should be emphasized that this technique, in general, provides information on the average microscopic structural parameters for the samples under investigation. Thus, if the colloidal particles contain differing structural units, or if samples contain defect sites attributable to different nucleation processes or mechanisms, it may not be possible to discern these differences.

Raman vibrational spectroscopy is a very powerful tool for obtaining both crystal-structure data to complement the above x-ray-diffraction results and molecular-structure data from which chemical-bonding information can be deduced. This technique is based on the inelastic scattering of incident laser light. The wavelength dependence of this scattered light is analyzed relative to the wavelength of the incident laser light to provide the Raman vibrational spectrum of the analyte. The crystal-structure data are inferred from the vibrational spectrum of the lattice vibrational modes (that is, those modes with energies typically below $\sim 200 \text{ cm}^{-1}$). The energies and intensities of these lattice modes provide information on crystallinity and long-range order in crystalline environments. The data on molecular structure are inferred from the vibrational spectrum of the internal vibrational modes (those modes deriving from the stretching, bending, and so forth, of chemical bonds). The bond-strength data can be calculated from the energies of these internal vibrational modes according to existing vibrational spectroscopic theory. As for the x-ray-diffraction method, if the colloids possess differing structural units or significant populations

of defect sites, these can mask or destroy the Raman lattice modes, making the data interpretation related to long-range order more complicated.

Electronic spectroscopy will also be used to characterize colloid structure to obtain information that complements the data obtained using the other more incisive techniques. This technique is essentially the same as that for the characterization of chemical reactivity. Namely, the characteristic transitions between the electronic energy levels in the colloid will be measured. However, more attention will be focused on the theoretical basis for the energies and intensities of the electronic transitions. Theory predicts that both the energies and intensities of the electronic transitions are strongly influenced by the crystal and molecular structural properties of the analyte. Extracting this structural information from the electronic spectra is complicated. However, it is plausible to deduce this information by comparing the electronic spectra of the colloids with those obtained for other species, such as binary oxides, that are well characterized. Furthermore, these data are easily obtained using existing, conventional instrumentation.

We will also use well-characterized, model radionuclide compounds for the other techniques being implemented in this structural characterization. This approach will greatly assist in interpreting the often complex structural data and will save considerable time by eliminating the need for detailed theoretical calculations. In fact, a semi-quantitative description of colloid structure (for example, identity of coordinating atoms, number of coordinating atoms, site symmetry) will be of great value in understanding and modeling the chemical reactivity of the colloids. For this reason, even though instrumental methods typically have a high level of accuracy, neither accuracy nor precision need be overwhelming concerns in this structural characterization.

It should be emphasized that the best approach that can be taken for the structural characterization of colloids is a combined one, in which many differ-

ent sources of data are considered in deriving the best possible description of the microscopic structure of the colloid species. Even if this approach falls short of a unique, explicit description, the effort is valuable. For example, the data might still be used to eliminate categories of potential structures from consideration, thereby enabling us to make better inferences concerning the sorptive properties of these species.

D. BATCH-SORPTION AND SORPTION-MODELING STUDIES

Objectives and Justification of Study

Purpose

The rock units in Yucca Mountain contain mineral and other solid phases known to have significant sorption affinities for most of the radionuclides likely to be emplaced in the potential repository (Daniels et al. 1982). These phases make up one of the multiple barriers to radionuclide migration in the potential repository block. The purpose of this study is to obtain data on the sorption behavior of key radionuclides under the physical and chemical conditions anticipated in the rock volume between the disturbed zone and the accessible environment. Here, key radionuclides are those radionuclides for which a sorption barrier could provide a significant contribution to the regulatory compliance strategy. For experimental purposes, the term “key radionuclides” is equivalent to the term “key elements” because all isotopes of a given element chemically behave essentially the same way. The key elements to be studied in this investigation include americium, carbon, cerium, cesium, iodine, niobium, nickel, neptunium, plutonium, radium, selenium, tin, technetium, thorium, uranium, and zirconium.

Data will be obtained that will provide input to the evaluation of alternative models for transport (for example, matrix versus fracture flow). Alternative models for sorption behavior will be investigated through studies on pure mineral separates. Key radionuclides that sorb dominantly by surface-complexation mechanisms will be studied in addition to radionuclides that sorb dominantly by ion exchange. Alternative models for transport will be addressed by studies of minerals that are found as fracture linings in Yucca Mountain and by studies on the sorptive potential of natural colloids in Yucca Mountain. Investigation of the sorption behavior of fracture-lining minerals will provide data on the impact of these minerals on the retardation of the important radionuclides during fracture

flow. The potential for the transport of radionuclides adsorbed onto colloidal materials will be investigated by studying the degree to which the important radionuclides sorb to natural colloids found in the Yucca Mountain groundwaters. Experimental investigation of the dynamic coupling of sorptive behavior with flow parameters is addressed in Investigation 8.3.1.3.6, Retardation by Dispersive, Diffusive, and Advective Transport.

Regulatory rationale and justification

The sorption data and models generated in this study will be one of the elements considered in evaluating whether or not the site meets the requirements of 10 CFR 60.112: Overall System Performance Objective for the Geologic Repository After Permanent Closure. This section states that the “geologic setting shall be selected . . . to assure that releases of radioactive materials to the accessible environment following permanent closure conform to such generally acceptable environmental standards for radioactivity as may have been established by the Environmental Protection Agency. . . .” Sorption is one of the mechanisms that might significantly affect the rate at which radionuclides are released to the accessible environment. 10 CFR 60.113(b) notes that the “geochemical characteristics of the host rock, surrounding strata, and groundwater” are one of the factors that the Nuclear Regulatory Commission might take into account in approving or specifying other radionuclide release rates, designed containment periods, or pre-waste-emplacement groundwater travel times that may be used in meeting the overall performance objective. The results of these studies will also be used in evaluating the favorable conditions of 10 CFR 60.122(b): Geochemical Conditions that (i) Promote Precipitation or Sorption of Radionuclides; (ii) Inhibit the Formation of Particulates, Colloids, and Inorganic and Organic Complexes that Increase the Mobility of Radionuclides; or (iii) Inhibit the Transport of Radionuclides by Particulates, Colloids, and Complexes. Similarly, the results of these studies will be used in evaluating the potentially adverse conditions of 10 CFR 60.122(c): Geochemical

Processes that Would Reduce Sorption of Radionuclides, Result in Degradation of Rock Strength, or Adversely Affect the Performance of the Engineered Barrier System.

The sorption data and models generated in this study will be used in the resolution of the following issues described in the Yucca Mountain Site Characterization Plan (SCP):

Issue	SCP Section
1.1	8.3.5.13
1.2	8.3.5.14
1.3	8.3.5.15
1.8	8.3.5.17
1.9	8.3.5.18
1.10	8.3.4.2

One of the supporting parameters needed in evaluating Issue 1.1 (SCP Table 8.3.5.13-17) is the sorption distribution coefficient (K_d) in the rock matrix for the following chemical elements: americium, carbon, cerium, cesium, iodine, neptunium, plutonium, strontium, technetium, uranium, and zirconium. This list has been expanded here because preliminary performance-assessment calculations indicated the need for sorption coefficients for other elements. These coefficients are to be provided for all hydrologic units in the controlled area. The performance-assessment (that is, total-system) calculations that are to be carried out for the resolution of Issue 1.1 are to include all credible scenarios for future events and processes at the Yucca Mountain site. For this reason, the resolution strategy for this issue, as it relates to sorption processes, can also be used in the resolution of the sorption-related questions in most of the other issues. However, for Issues 1.8 and 1.9, the resolution strategies call for expert professional judgment and other calculations in addition to the total-system calculations. The resolution strategy for Issue 1.5 (Waste Package and Engineered Barrier Performance Evaluation, SCP 8.3.5.10) calls for a set of hydrothermal sorption experiments independent of this task. Near-field sorption is not addressed in this study plan.

The Nuclear Regulatory Commission (NRC), in its “Generic Technical Position on Sorption,” has drawn attention to a number of potential problems in the interpretation and application of batch-sorption data. These problems concern aspects of the experimental technique and application of the results to real-world situations. Data obtained in this task will be combined with data obtained in Investigation 8.3.1.3.6 (Retardation by Dispersive, Diffusive, and Advective Transport) to address the concerns of the NRC.

Rationale

Technical rationale and justification

Approach

The derivation of sorption ratios appropriate to the entire range of scenarios to be considered for post-closure performance assessments would require experiments that address all the values of the dominant physical and chemical variables involved in the scenarios. The number of separate experiments required to address directly all the variables over their estimated ranges would be unrealistically large. Further, this approach would provide little in the way of predictive capability to address scenarios not included in the experimental matrix. With an eye towards a more pragmatic approach, a sorption strategy has been developed that is based on sound chemical principles, requires a smaller number of experiments, and provides a basis for prediction of the sorption behavior of the key radionuclides.

In this strategy, the key radionuclides are divided into three groups on the basis of what is known about their affinity for the types of solid surfaces available in rocks from Yucca Mountain. The groups are 1) high-affinity, 2) low- to intermediate-affinity, and 3) “no-affinity.” Radionuclides in the high-affinity group should have sufficiently large sorption coefficients (say, > 100 ml/g), even in the worst-case flow scenarios, so that regulatory constraints can be met in any case. Therefore, knowledge of the exact value of the sorption coefficient for each of these radionuclides at any point in the

flow system will not be critical and a minimum K_d value should suffice. Which of the key radionuclides are in this group will be determined through experiments involving the most reactive water composition identified in Yucca Mountain for each of the key radionuclides and the least-sorptive rock composition as identified on the basis of the pure mineral studies discussed below. Out of the range of compositions expected in Yucca Mountain, the most reactive water composition is that which yields the highest concentration of the radionuclide in solution. Those radionuclides having no affinity for the solid surfaces in rocks from Yucca Mountain will not have a sorption barrier. These radionuclides will also be identified on the basis of whole-rock and pure mineral experiments.

The radionuclides with low to intermediate affinities for the rock surfaces in Yucca Mountain will require the most detailed evaluation. They will initially be identified by failing to fall into either the high- or no-affinity groups. Once identified, their sorption behavior will be investigated through additional experiments on pure-mineral separates in which the major solution (groundwater) compositional parameters (for example, pH) are varied over the ranges of values anticipated in the Yucca Mountain flow systems. These experiments and any pertinent information that may be available in the literature will be used to identify those solution parameters that most affect the sorption behavior of each of the low- to intermediate-affinity radionuclides.

Once these “controlling” solution parameters have been identified, a series of whole-rock experiments will be performed involving representative samples from each of the hydrologic units identified at Yucca Mountain and representative groundwaters in which the controlling solution parameters for each radionuclide are varied over the ranges expected within Yucca Mountain. The term “representative” refers to samples with compositions within the range seen in the field. Attention will also be given to parameters that have a large effect in sorption as determined by experiments and cal-

culations. By combining the results of these experiments with probability distributions for the controlling groundwater compositional parameters, probability distributions for the sorption coefficients for these radionuclides will be derived for each of the hydrologic units.

The pure mineral experiments used to derive the high-, low-to-intermediate-, and no-affinity groupings can also be used in estimating sorption coefficients for fracture linings as a function of the surface area and fracture water compositions, assuming these data are available. If the dominant sorption mechanisms can be determined in the pure mineral experiments with each radionuclide, a basis for the prediction of sorption behavior would be developed that would aid in the evaluation of scenarios that are not under consideration at the present time but may become significant in the future.

Types of measurements to be made

The measurements to be made in this study (Studies 8.3.1.3.4.1 and 8.3.1.3.4.3) make up the following SCP Activities:

- batch-sorption measurements as a function of solid-phase composition (8.3.1.3.4.1.1),
- batch-sorption measurements as a function of sorbing-element concentrations (isotherms) (8.3.1.3.4.1.2),
- batch-sorption measurements as a function of groundwater composition (8.3.1.3.4.1.3), and
- batch-sorption measurements on particulates and colloids (8.3.1.3.4.1.4).

Rationale for types of measurements

Rationale for the selection of techniques. The basic technique selected for the four activities listed above is the batch-sorption experiment in which the distribution of a radionuclide between a solution phase (for example, groundwater) and a crushed or powdered sample is measured as a function of any number of variables. This technique is valuable because it is simple and a large number of samples can be processed in a relatively short time. By varying the solid composition, the solution composition, the atmospheric composition, the

radionuclide concentration, or the physical conditions (such as temperature) at which the experiment is conducted, sorption ratios can be determined for the various scenarios anticipated for the proposed repository in Yucca Mountain.

Alternative techniques for the derivation of sorption coefficients include the batch-wafer technique, column-migration experiments, field-migration experiments, and natural-analog studies. The batch-wafer technique and column-migration studies are described in the study plan for Investigation 8.3.1.3.6 (Retardation by Dispersive, Diffusive, and Advective Transport). The batch-wafer technique provides the same sort of data as the crushed-rock method. However, because of slow diffusion kinetics, particularly for the actinide elements, this technique requires considerably more time to achieve sorption equilibrium. Although column-migration experiments can also yield sorption coefficients under ideal conditions, they involve a greater number of variables (for example, flow rate, dispersion, and diffusion) than batch experiments. For this reason, batch experiments are often required to interpret column experiments. Field-migration experiments are described in the study plan for Reactive Tracer Field Test Activities (Study 8.3.1.3.7.2). In terms of the derivation of sorption coefficients, field-migration experiments suffer from similar problems as the column-migration experiments, only to a greater degree. Unique values for sorption coefficients are very difficult to derive from field-migration studies. Natural-analog studies can potentially provide information on the sorption behavior of a given radionuclide in the natural environment. However, because a sufficiently detailed database on the spatial and temporal variations in critical environmental parameters (such as pH, Eh, and groundwater composition) that determined the migration behavior of a given radionuclide at an analog site are rarely available, sorption coefficients derived from such studies are of qualitative value at best.

There are several new state-of-the-art experimental techniques that are being used in the surface-sci-

ence community to investigate the detailed chemical and physical nature of sorption reactions. These include extended X-ray absorption fine-structure analysis (EXAFS), photoacoustic spectroscopy (PAS), and scanning-tunneling/atomic-force microscopy (STM/AFM). In addition, there are other more established techniques that are used to study the composition and reactivity of surfaces including time-of-flight secondary-ion mass spectroscopy, ion-beam analysis, and microcalorimetry. Some or all of these techniques may be of use in the development of a basic understanding of the adsorption behavior of the key radionuclides on Yucca Mountain rock and mineral surfaces. Such understanding could be important to the development of robust predictive models for the sorption behavior of these radionuclides under conditions not addressed directly in the experimental program outlined below.

Rationale for the selection of tests

The tests and analyses to be carried out in this investigation include the following:

- sorption measurements as a function of rock composition and sorption measurements on pure mineral phases (Activity 8.3.1.3.4.1.1),
- sorption measurements as a function of sorbing-element concentrations (isotherms) (Activity 8.3.1.3.4.1.2),
- sorption measurements as a function of groundwater composition (Activity 8.3.1.3.4.1.3), and
- sorption measurements on particulates and colloids (Activity 8.3.1.3.4.1.4).

As noted above, the strategy developed to obtain sorption coefficients for performance-assessment calculations assigns the important radionuclides into one of three groups according to the affinity of each radionuclide for the mineral and other solid surfaces present in the hydrologic units delineated within Yucca Mountain. In the first activity listed above, experiments will be conducted to allow assignment of each of the important radionuclides into one of the three groups. For radionuclides with high affinities for the rock surfaces, these

experiments will provide the basis for the assignment of minimum K_d values to be used in performance-assessment calculations. These values will reflect conservative assumptions concerning water compositions (that is, the most-reactive water compositions) and the sorption potential (that is, least-sorptive) of various solid surfaces in Yucca Mountain. The most-reactive water compositions will be identified on the basis of all pertinent data available in the literature concerning the radionuclides of interest and a limited number of experiments with different water compositions as discussed further below. The least-sorptive mineral and rock surfaces will be identified in the pure mineral experiments. For many of the high-affinity radionuclides (for example, americium, cerium, niobium, radium, tin, thorium, and zirconium), the experiments will involve solution concentrations near the solubility limit as these elements have low to very low solubilities in near-neutral waters. This fact means isotherms will not be required for these elements.

Those radionuclides for which no reliable (positive) sorption coefficient can be demonstrated in whole-rock experiments, when using the least-reactive groundwater and the lowest-reasonable solution concentrations, will not be investigated further by this study.

The second and third activities listed above will concentrate on those elements that have relatively high solubilities and low to high sorption potentials in Yucca Mountain groundwaters. The experiments will be divided into two groups: one for high-affinity/high-solubility radionuclides and the other for low-affinity/high-solubility radionuclides.

The high-affinity/high-solubility group will likely include the element cesium and possibly the element nickel. Isotherm experiments with these elements will involve a minimum-sorbing rock type from each of the hydrologic units, the groundwater composition with the highest ionic strength, and concentrations up to the maximum values expected to be released from the engineered-barrier system. If the minimum K_d value measured in these experi-

ments is sufficiently large, as evaluated by transport calculations in Study 8.3.1.3.7.1, Retardation Sensitivity Analysis, no further experiments will be carried out with these elements. On the other hand, if the measured value of K_d is not sufficiently large for either of these elements, the element will be assigned to the low-affinity/high-solubility group.

The low-affinity/high-solubility group is the most challenging in terms of the characterization of sorption behavior in a complex system such as the Yucca Mountain hydrologic flow system. The elements in this group will likely include uranium, neptunium, selenium, and possibly plutonium and nickel. Addressing the sorption behavior of this group will require the evaluation of couplings between three of the four activities listed above.

First, the (aqueous) solution parameters that have the greatest influence on the sorption behavior of each element will be identified through experiments with pure mineral separates of the major and some of the minor phases identified in Yucca Mountain rocks (Activity 8.3.1.3.4.1.1). The identities and ranges of the solution parameters to be considered will be obtained from literature reviews and from Investigation 8.3.1.3.1, Water Chemistry. Second, experiments will be performed for each of the low-affinity elements involving representative rock samples from each of the hydrologic units identified at Yucca Mountain and several groundwaters representing each of the major groundwater types identified at Yucca Mountain. The values of those solution parameters (such as pH) that were identified as having a significant influence on the sorption behavior of a given element will be varied in each groundwater over the ranges anticipated in Yucca Mountain. Third, isotherms will be obtained on a subset of the previous experiments. Finally, the resulting database will be used in conjunction with probability distributions for each of the dominant groundwater compositional parameters and radionuclide source-term concentrations to obtain probability distributions for the K_d values for each of the low-affinity/high-solubility elements in each hydrologic unit within Yucca Mountain. This

activity will be part of Study 8.3.1.3.4.3, Development of Sorption Models.

The data resulting from the experiments involving pure-mineral separates and groundwaters from Yucca Mountain could also be used to estimate values of K_a (surface-area-based sorption coefficients) for fracture-lining minerals, assuming data are available on the distribution and accessibility of fracture coatings and on the composition of fracture waters.

If sorption of radionuclides occurs on colloids or other particulates and if those colloids and particulates could be transported by groundwater to the accessible environment, then the use of sorption coefficients alone may not adequately predict the transport of the radionuclides. Transport could occur on naturally occurring colloids and particulates present in groundwater (SCP 4.1.2.7), on material created by the degradation of components of the engineered-barrier system (SCP 8.3.5.10), or by microbes (SCP Study 8.3.1.3.4.2) present in groundwater or introduced into the repository during construction or operation. Experiments on the sorption of key radionuclides will be carried out in this investigation once the likelihood and the mechanisms of colloid or particulate transport in the repository environment have been demonstrated by Investigation 8.3.1.3.6, Retardation by Dispersive, Diffusive, and Advective Transport.

Constraints

Constraints on these investigations include the availability of adequate information on 1) the ranges of water compositions, including pH and Eh and organics, expected in each hydrologic unit over the lifetime of the potential repository (Investigation 8.3.1.3.1, Water Chemistry), 2) the identification and spatial distribution of major, minor, and trace minerals in each of the hydrologic units defined within the site (Investigation 8.3.1.3.2, Mineralogy, Petrology, and Chemistry), 3) the solubilities of each of the key radionuclides in Yucca Mountain groundwaters (Investigation 8.3.1.3.5, Retardation by Precipitation), 4) the radionuclide

source term from the engineered-barrier system (SCP 8.3.5.10), and 5) the identity and thermodynamic characterization of the chemical species (for example, complexes) of the key radionuclides in groundwaters at Yucca Mountain (Activity 8.3.1.3.5.1.2, Radionuclide Speciation Measurements). The availability of suitable solid samples and groundwaters are another constraint.

Some data are available on each of these constraints at the present time and more will become available as the site characterization program goes forward. The experimental program in this investigation will start on the basis of the existing database and branch out as new information becomes available. For instance, once adequate data become available on the compositions of unsaturated-zone waters at or below the potential repository level, experiments with this water composition will be initiated. This will eventually result in an understanding of sorption processes that can be used to support alternative conceptual models, including the multiple-barrier approach to containment.

Effect on the site

Analyses necessary for this investigation should have minimal impact on the site because most of the necessary samples will be obtained from planned drill holes or existing core. The groundwater samples will be obtained from either existing or planned wells in the area. Additional core samples and water samples from the unsaturated zone will be requested, if available, during construction of the exploratory studies facility. No sampling requirements or procedures are needed over and above those already in place.

Required accuracy and precision

The performance goals and confidence levels set for sorption coefficients for the key radionuclides in the Site Characterization Plan (that is, SCP Table 8.3.5.13-17) are minimal and should be easy to meet given our current knowledge. Because new performance goals and confidence levels have not yet been defined, the accuracy and precision required to meet these goals and levels cannot be

defined. In the interim, the accuracy and precision goals will be defined to be consistent with the strategy discussed in the section above on “Rationale for the selection of tests.”

The accuracy and precision with which sorption coefficients for the key elements are to be measured are mainly a function of the group to which the element has been assigned. Those elements in the high-affinity group must have K_d values that exceed the minimum K_d when all associated errors (two standard deviations) are taken into account. For instance, if the measured K_d is 1000 ml/g and the desired minimum K_d value is 100 ml/g, the maximum error allowed in the measurement of the K_d would be ± 900 ml/g at the 1.0 confidence level. To be conservative, a smaller error would be preferred, allowing a lower confidence level. For those radionuclides in the no-affinity group, error estimates are not required unless credit is taken for the small positive values of K_d that may be measured in some experiments. In this case, the error levels would likely be determined by the capability of the experimental technique. If the error levels associated with the technique are too large to allow the assignment of a positive value for the K_d , a value of zero would have to be assigned to the K_d for the element.

The accuracy and precision required for the low- to intermediate-affinity elements are more difficult to define because of the probabilistic nature of the assignment of the value of K_d . The best that can be done is to include the experimental errors associated with the measured K_d values, for a given element in a given hydrologic unit, in generating the probability distributions for that K_d .

Simulation of repository conditions

The studies in this investigation are designed to address the sorption behavior of radionuclides in the far field (that is, outside the disturbed zone of the potential repository). Sorption in the far field represents one of the multiple barriers to radionuclide transport between the potential repository and the accessible environment. No effort is made in

this investigation to simulate near-field conditions (that is, inside the disturbed zone of the repository). Efforts will be made, however, to address present and future variations in far-field conditions, such as atmosphere, groundwater composition, mineralogy of the host rock, and temperature, to the extent that these conditions can be defined by other investigations. The “sorption strategy” discussed in the introduction to this section will be used to decide to what extent actual conditions, as opposed to bounding conditions, should be replicated in the experiments.

The NRC (1987) has expressed concern regarding the use of crushed-rock samples versus solid-rock samples from Yucca Mountain in the batch-sorption experiments. The concern is mainly that crushing of the rock material could result in the formation of particularly reactive sites on the surfaces of the crushed material. Because these “sites” would not be present in solid rock in the far field of the potential repository, they could inject a nonconservative bias into the experimental results if radionuclides were preferentially bound to these “sites” in the laboratory experiments. Fortunately, data obtained to date suggest that the use of crushed materials may not be a serious problem for sorption experiments involving tuffaceous rocks. For example, Rundberg (1987) has shown that sorption coefficients obtained for alkali and alkaline-earth elements on crushed tuff were essentially equal to coefficients obtained for these elements on solid wafers of the same tuffaceous samples. There are at least two reasons why this may be the case. First, the crushed-rock samples are preconditioned with the background water composition that is to be used in the sorption experiments. This procedure allows any “active sites” that may have been produced in the crushing process to pre-react with the chemical constituents in the water. Second, the matrices in the tuffaceous rocks of Yucca Mountain are very fine grained ($< 1\text{--}5\ \mu\text{m}$). Therefore, crushing to a 75- to 500- μm grain size results mainly in the separation of crystals along pre-existing grain boundaries. In contrast, for coarser-grained rocks (for example, granites),

crushing would result in the fracturing of individual crystals, leading to the creation of new grain boundaries. To investigate whether or not crushing has an effect on the values obtained for sorption coefficients of other elements (such as the actinides), solid-wafer/crushed-rock paired experiments involving these elements will be carried out in coordination with Investigation 8.3.1.3.6, Retardation by Dispersive, Diffusive, and Advective Transport.

The NRC (1987) also expressed concern over the large water/rock ratios used in the YMP sorption experiments relative to the water/rock ratios likely to exist in Yucca Mountain. It appears the impact of variable water/rock ratios on sorption coefficients can be modeled by isotherm equations. In effect, a high water/rock ratio simply means there is more of the radionuclide available in the solution phase for sorption onto the solid phase. If the radionuclide has a nonlinear isotherm, this leads to smaller sorption coefficients in experiments with higher water/rock ratios. This result suggests that the batch-sorption experimental technique used in the YMP should lead to conservative values for sorption coefficients.

Another aspect of the experimental technique that may result in conditions different than those in the rock volume near the repository concerns the degree of saturation of the host rock. The batch experiments are carried out under saturated conditions, whereas the potential repository horizon is located in the unsaturated zone. Two observations are pertinent with regard to this issue. The first is that there is no reason to suspect that sorption reactions between groundwater and rock/mineral surfaces under unsaturated conditions (70–80% saturation) would be significantly different from sorption reactions that take place under saturated conditions, assuming the background water compositions are the same. Groundwater compositions used in the batch-sorption experiments will bound the compositions found in the unsaturated zone. The second observation is that unsaturated column experiments will be conducted in the Dynamic

Transport Investigation (SCP 8.3.1.3.6). These experiments will provide further tests of the applicability of the (saturated) batch experiments to unsaturated flow conditions.

Another further aspect of the experimental technique that may result in conditions somewhat different from those in the potential repository environment concerns the number of radionuclides present in a given batch experiment versus the number and concentrations of radionuclides present in the solutions that may emanate from the engineered-barrier system (that is, the source term) of a potential repository. There will likely be more radionuclides in the repository source term compared to the batch experiments. The question is, how will this aspect be integrated into the K_d values used in performance-assessment calculations? To answer this question in a quantitative manner, we would need data on the sorption capacity of all the rock/mineral surfaces in Yucca Mountain rocks, the relative affinities of all the radionuclides and the natural chemical constituents in groundwater for these rock/mineral surfaces, and the concentrations of all chemical constituents in the groundwaters, as well as other parameters. In the following, we develop a more pragmatic approach for use in this investigation.

Because most of the key radionuclides are isotopes of elements that have low to very low solubilities in Yucca Mountain groundwaters and have high to very high affinities for the rock/mineral surfaces in Yucca Mountain, the maximum total concentration of these elements in solution will generally be low. For the purposes of this investigation, this group of radionuclides can be thought of as a single component with a concentration equal to the total concentration of the separate radionuclides in solution. The sorption coefficient for this hypothetical component may be smaller than the coefficients for the individual radionuclides because of the higher concentrations involved (that is, the hypothetical sorption coefficient would be higher up along some sort of composite isotherm). However, as long as the minimum value of K_d for the high-affinity ele-

ments is less than the value of the K_d for the hypothetical component, no problems should arise involving retardation of these elements in the performance-assessment calculations. Experimentally, the composite isotherm could be measured for a given radionuclide by using solutions saturated with nonradioactive compounds of the other high-affinity radionuclides or appropriate analogs.

The radionuclides representing the elements carbon, iodine, and technetium have very low affinities for rock/mineral surfaces in Yucca Mountain; therefore, they will not compete successfully with other radionuclides for sorption sites. The migration rate for these radionuclides will be determined primarily by physical processes (for example, dilution, diffusion, and so forth). This leaves radionuclides of the elements uranium, neptunium, nickel, cesium, selenium, and plutonium for further consideration. The element cesium has higher affinities for zeolitic rocks than any of the other key radionuclides or of the major constituents of Yucca Mountain groundwaters. This suggests zeolitic units will be the primary barriers for cesium migration in Yucca Mountain, although other units will also retard cesium to a lesser degree.

The sorption coefficients measured for nickel in Yucca Mountain groundwaters are generally greater than 100 ml/g. These results are consistent with the fact that nickel is known to be strongly sorbed by soils and suggests that nickel competes favorably with the major groundwater constituents for available surface sites but not as favorably as the high-affinity elements. Therefore, the value of its K_d in the high-affinity, element-enriched zone around the waste package may be smaller than that measured in batch experiments with single radionuclides. In the far field, however, the batch K_d values should be appropriate. The element nickel is known to be strongly sorbed on soils. The fact that the total inventory of nickel will be small relative to the actinide elements is also a significant consideration.

The key radionuclides representing the elements

uranium, neptunium, and selenium likely will not compete successfully for sorption sites with the high-affinity radionuclides. In the zone of high-affinity elements near the waste packages, the K_d values for these radionuclides may be smaller than those measured in typical (single radionuclide) batch experiments unless multilayer adsorption (for example, surface precipitation) is a significant process. Outside this zone, the K_d values for uranium, neptunium, and selenium will be determined by competition for sites among themselves and with the natural chemical constituents of the groundwater. By using groundwaters from the site in the batch experiments, the competitive effects involving the natural constituents are accounted for. This approach leaves the competitive effects between the radionuclides and the natural constituents in solution as the main parameters to be determined. The most straightforward way to determine these parameters is to carry out batch experiments containing all three of these elements.

Plutonium will be the most difficult to characterize in terms of sorption potential because it does not consistently appear to be a high-affinity element in relation to Yucca Mountain rock/mineral surfaces. Interestingly, this fact is in contrast to observations that found plutonium to be a very-high-affinity element on most common mineral surfaces (such as quartz, montmorillonite, and biotite). In any case, plutonium has much higher affinities (an order of magnitude or more) for rock/mineral surfaces in Yucca Mountain than elements such as uranium, neptunium, and selenium. The simplest approach for dealing with plutonium sorption would be to ignore any sorption of that element in the high-affinity zone close to the waste package and carry out batch experiments also containing uranium and, possibly, neptunium. Because uranium and neptunium have similar sorption coefficients on Yucca Mountain rock/mineral surfaces and because plutonium has a much higher affinity for Yucca Mountain rock/mineral surfaces, the presence of only one of these elements (such as uranium) at a concentration near its solubility limit may be sufficient to gauge competitive effects with plutonium.

This would minimize the radiation exposure to the analyst.

A final issue relating to simulation of repository conditions concerns the possible influence of organic coatings on rock/mineral surfaces and organic complexes in the Yucca Mountain groundwaters. The concentrations of organic constituents in these waters appear to be very low (< 3 ppm). However, no data are available on the presence or absence of organic coatings on rock/mineral surfaces in Yucca Mountain. By using rock and water samples from the site in the whole-rock sorption experiments, the possible influence of organics will be accounted to a significant, although quantitatively undetermined, extent.

Capability of analytical methods

The analytical methods used in this investigation are well established (see Table 2 in Chapter I) and fully capable of generating the required information, given proper concern for potential experimental artifacts. Potential artifacts include: 1) oversaturation of the solution with a compound of the radionuclide of interest, 2) incomplete solid-liquid separations, 3) adsorption of the radionuclide of interest to the walls of the experimental container, 4) incomplete equilibrium between species in solution, and 5) incomplete sorption equilibrium.

The oversaturation question can be addressed using the experimental solubility results of Investigation 8.3.1.3.5, Radionuclide Retardation by Precipitation, and pertinent literature data. Questions concerning incomplete separations and adsorption to container walls are addressed in the current batch procedure. Equilibrium between species in solution and in the sorption reactions cannot be directly tested. The approach taken on these equilibrium questions in previous work (for example, Daniels et al. 1982) consisted of time-series experiments in which the same experimental system was allowed to “equilibrate” over a range of time intervals until a steady-state value was achieved for the distribution coefficient R_d . This steady-state value was called the K_d . The time required to reach steady

state was generally less than six weeks. This time interval will be the duration of the batch experiments carried out in this investigation.

Time required versus time available

Using the strategy detailed above (in “Simulation of repository conditions”) for the derivation of sorption coefficients for performance-assessment calculations, the time required to complete this investigation will depend mainly on the success of the experimental program, staffing, and so forth. There is no reason to believe this investigation could not be completed in 5 to 6 years.

Limitations of equipment and applicability to field

The test planned for this investigation will not be limited by equipment capabilities or availability.

Questions relating to the applicability of the sorption coefficients measured in this investigation to the field are discussed above in “Simulation of repository conditions.”

Questions relating to the applicability of batch-sorption coefficients to the field are also addressed by the dynamic-transport experiments in Investigation 8.3.1.3.6, Retardation by Dispersive, Diffusive, and Advective Transport.

Interference with other tests

The laboratory experiments carried out in this investigation will not interfere with other tests.

Limitations on repeatability of tests

The primary limitation on the repeatability of tests planned for this investigation is the availability of appropriate rock and groundwater samples from the site of the potential repository.

E. DYNAMIC TRANSPORT STUDIES

Purpose and Objectives of Studies

Purpose

As described in Study 8.3.1.3.6.1 (Dynamic Transport Column Experiments) of the Site Characterization Plan (SCP), the purpose of this study is to provide data to predict the potential for radionuclide movement from the repository to the accessible environment. The principal intent of these studies is to test the necessary assumptions made in applying values of the sorption distribution coefficient, K_d , (determined by the batch-sorption measurements described in Study 8.3.1.3.4.1, Batch Sorption Studies) to describe hydrologic transport. These assumptions are that 1) microscopic equilibrium is attained between the solution species and the adsorbent, 2) there is only one soluble chemical species or, if more than one species is present, the species interchange rapidly and are present in the same properties, 3) the radionuclides in the solid phase are adsorbed on mineral surfaces, that is, not precipitated, 4) the dependence of sorption on concentration is described by a linear isotherm, and 5) crushing the rock does not alter the sorption properties.

The importance of verifying these assumptions can be demonstrated by the following hypothetical cases. 1) If equilibrium were not attained in the batch experiments, the retardation of radionuclides could be dependent on groundwater velocity. Some mineral-forming reactions can occur that incorporate adsorbed radionuclides in the crystal structure in an irreversible manner. Such reactions would increase the value of the distribution coefficient on a geologic time scale, that is, batch measurements would determine conservative values of sorption. Mineral changes induced by differences in exchangeable cation compositions, on the other hand, could lead to lower values of K_d on geologic time scales. These reactions are studied under SCP Activities 8.3.1.3.2.2.1, History of Mineralogic and Geochemical Alteration of Yucca Mountain, and 8.3.1.3.2.2.2, Smectite, Zeolite, Manganese Mine-

als, Glass Dehydration, and Transformation. 2) If a radionuclide were present in solution as two different species, an anion and a cation, and solution equilibrium were not maintained, the batch measurement would predict a single retardation factor. Whereas, in a flowing system, the anion would move unimpeded because of the paucity of anion-exchanging minerals in Yucca Mountain tuff. 3) If the radionuclide had precipitated in the batch experiments, the K_d value thus determined would be meaningless. Depending on the precipitation mechanism, colloid transport could be important. 4) A nonlinear isotherm will usually result in broadening of the migration front of radionuclides in column studies. This effect would appear as increased dispersion over that observed for non-sorbing tracers. 5) If crushing tuff were to expose reactive mineral surfaces that were unavailable in the intact tuff, retardation in the field would be lower than batch measurements would predict.

The studies described in this plan will provide an experimental basis for validating transport models. The experiments are designed to vary in complexity from crushed tuff, which has the most similarity to the batch measurements (that is, would not test assumption 5 listed above), to solid tuff and fractured tuff, in which steady state is not achieved during the course of the experiment. In all the experiments described under this activity, the physical processes include the following: advection, dispersion (which is minimized in the crushed-tuff experiments), and diffusion (both longitudinal, in the crushed- and solid-tuff columns, and transverse in the fractured-tuff columns). The advective process can be further subdivided into saturated and unsaturated components. The dispersion and diffusion coefficients are also expected to vary with saturation, and these effects will be studied in unsaturated-flow experiments.

Validation of transport models will be effected in conjunction with Investigation 8.3.1.3.7, Radionuclide Retardation by All Processes along Flow Paths to the Accessible Environment. The transport experiments, varying in complexity, will be

modeled using the transport processes currently available in the transport codes of Investigation 8.3.1.3.7. If the outcome of these efforts indicates that the transport codes are ignoring processes that are essential to the prediction of transport behavior as shown by the experimental results, the identified processes will be added to the transport models used. This type of effort will lead to a cycle of modeling and experimentation, which should identify the key experiments to be performed as well as improve the transport models used.

Use of results

This study is part of Investigation 8.3.1.3.6, which will determine experimentally the rate of movement and effective retardation of radionuclides by dispersive, diffusive, and advective processes. The data generated by these studies will be used as input to the Geochemical Test Program described in the SCP Overview 8.3.1.3 and the related performance issues: 1.1 Total System Performance (SCP Section 8.3.5.13), 1.2 Individual Protection (SCP Section 8.3.5.14), 1.3 Ground Water Protection (SCP Section 8.3.5.15), and 1.8 NRC Siting Criteria (SCP Section 8.3.5.17). The confidence level required for the geochemical retardation performance parameter (due to sorption) to be determined in this study is high (SCP, p. 8.3.1.3-16). The confidence level required for the geochemical retardation performance parameter (due to dispersion and filtration of colloids) is high for the unsaturated zone and medium for the saturated zone (SCP, p. 8.3.1.3-17).

The results of this study will provide confirmation of the validity of the sorption data generated in Investigation 8.3.1.3.4, Radionuclide Retardation by Sorption Processes, for application to flowing conditions. Specifically, Issue 1.1, Total System Performance (SCP Section 8.3.5.13), requires experimental evidence that could confirm or deny the theory of advective-diffusive coupling of solute concentrations in matrix and fracture fluids, which is currently embodied in the transport model of TOSPAC. Issue 1.1 states that this information is crucial in establishing the credibility of transport

phenomenology embodied in any model used to assess the consequences of the release scenarios associated with water pathways. This investigation will also provide information on the transport of colloids and the validation of data produced in saturated systems for application to an unsaturated system.

Rationale

Approach

We will study the migration of radionuclides and nonradioactive analogs to waste elements through tuff samples under a variety of conditions. The experiments are intended to investigate the effects of kinetics, dispersion, diffusion, and speciation on the transport of radionuclides, which could alter the level of detail required to model repository performance. The experiments to be performed range in complexity from crushed tuff, in which the tuff is nearly identical in composition and physical form to tuff samples used in batch-sorption experiments and hydrodynamic dispersion is minimal, to fractured-tuff columns, in which the transport is affected by channeling, matrix diffusion, and the processes affecting transport in the crushed-tuff columns. To accomplish this, we have subdivided our efforts into the following activities:

- Crushed-tuff column studies will be performed to verify the results of batch-sorption measurements under flowing conditions without significantly changing the surface properties of the tuff. By measuring differences from the batch measurements, these studies would be most sensitive to multiple-species formation, colloid formation, and any other geochemical reactions (for example, changes in surface reactivity due to agitation) not adequately described by batch distribution coefficients measured in Investigation 8.3.1.3.4, Radionuclide Retardation by Sorption.
- Previous results indicate that plutonium and, to a lesser extent, americium show a change in sorption distribution coefficient as a function

of time. This study concluded that the kinetics of actinide sorption on Yucca Mountain tuff needed to be studied in more detail.

Mass-transfer kinetics studies using crushed-tuff columns will be performed to investigate the migration of radionuclides as a function of water velocity. The broadening of the elution curves depends on the velocity of the water, with hydrodynamic dispersion and kinetics having a different dependence on velocity. Therefore, the velocity dependence of the elution curve will provide rate constants if a velocity dependence is observed. The results obtained from these experiments will be compared with similar results to be obtained under static conditions using tuff wafers and rock beakers in Study 8.3.1.3.6.2, Diffusion.

- Unsaturated-tuff column studies will be performed to investigate the transport of radionuclides through intact tuff columns at various degrees of saturation. These studies will measure the retardation factor for sorbing radionuclides in intact tuff as a function of saturation, addressing the question of whether crushing affects sorption. The dispersion will also be measured as a function of saturation to determine how tortuous the flow path becomes and whether the mineralogy along the path changes with water content.

The applicability of the parameters obtained under saturated conditions to unsaturated conditions will be assessed. The parameters (such as sorption distribution coefficients) determined under saturated conditions will be used to predict transport behavior under unsaturated conditions to assess whether additional parameters inherent in unsaturated conditions need to be determined and what the processes are that drive transport in the unsaturated zone. The models describing radionuclide transport under unsaturated conditions (developed in Investigation 8.3.1.3.7, Radionuclide Retardation by All Processes) will be tested using the results of experiments describing

transport in unsaturated tuff (such as the ones performed in this study).

- The tuff of Yucca mountain contains several welded units that have high fracture densities and low matrix permeabilities. The saturated zone is known to be most transmissive in these welded fractured zones, and episodic water movement through fractures in the unsaturated zone has not been ruled out. Fractured-tuff columns will be used to investigate the transport of radionuclides with transverse matrix diffusion and channeled flow in fractures. Saturated flow in fractures with an unsaturated matrix will be investigated to examine the transport of radionuclides by ephemeral water movement.
- Filtration studies will examine the efficacy of tuff to filter or adsorb colloids of various sizes and surface charge. These experiments will be performed both on fractured and unfractured tuff samples.

Types of measurements to be made

The types of measurements that will be made include tracer concentrations in initial and eluted solutions using 1) gamma-ray spectrometry, 2) liquid-scintillation counting, 3) alpha spectrometry, 4) fluorometry, 5) visible absorption spectrometry, and 6) autocorrelator photon spectrometry. The porosity of rock matrices will be determined by weight difference between saturation and dryness. Free column volumes will be determined by the elution of tritiated water. Fracture surface topography will be determined by stylus profilometry, and the flow path will be determined by autoradiography of fracture surfaces after elution. The analytical techniques used in these tests are standard techniques for acquisition of these types of data. Ancillary measurements will include: bulk-rock and fracture-surface mineralogy (described in Study 8.3.1.3.2.1, Mineralogy, Petrology, and Chemistry of Transport Pathways) and batch-sorption distribution coefficients (described in Study 8.3.1.3.4.1, Batch-sorption Studies).

Rationale for choosing the types of measurements to be made

Most of the information that can be gained from the transport experiments is contained in the shape and retention volume of elution curves. The elution curve is the tracer concentration as a function either of time or of the volume eluted from the column. The concentration of tracer is determined by the appropriate analytical technique. For example, a radioactive tracer having a unique gamma-ray energy is best analyzed by gamma-ray spectrometry. Pure beta emitters, such as tritium, are best analyzed by liquid scintillation, and alpha emitters by alpha spectrometry. Fluorometry will be used to measure the concentration of polystyrene latexes, which have been tagged with fluorescent dyes. Untagged latexes will be analyzed by autocorrelator photon spectroscopy. Colored dyes will be analyzed by visible absorption spectroscopy. Matrix porosity of solid-tuff samples will be determined by measuring the difference between the saturated weight and the air-dried weight.

Constraints for the study

One of the most significant constraints on this study is the extent of knowledge of potential transport pathways away from the proposed repository. An important goal of this study is to characterize accurately and completely the transport behavior of radionuclides under conditions that allow the identification of important geochemical and transport processes and mechanisms so that the appropriate models can be employed to predict transport in the field.

For strongly sorbing radionuclides, measuring elution curves may be extremely difficult. In this case, the tuff columns will be sectioned, and the distribution of radionuclides along the column will be obtained. Although this is a constraint on the proposed studies, if the radionuclide sorbs so strongly to tuff that no break-through can be detected, then it is safe to assume that the very high value of K_d , expected from batch-sorption studies, is representative of the value of K_d that should be used for performance-assessment calculations.

Another constraint is the lack of knowledge of the chemical speciation of actinides under groundwater conditions. The solubility studies (Study 8.3.1.3.5.1, Dissolved Species Concentration Limits, and Study 8.3.1.3.5.2, Colloid Behavior) will address this limitation. The studies outlined in this plan do not include oxidation-reduction reactions as a significant process. This decision was justified because locating the repository in the unsaturated zone will generally provide oxidizing conditions. The discovery of an unusual sensitivity to oxidation potential would require the inclusion of additional experiments.

Additional factors for consideration

Impact on site

The analyses initiated by this study should have minimal additional impact on the site because most samples necessary for the study will be obtained from cores from existing and planned drill holes or from surface outcrops. Large samples for evaluating radionuclide transport through fractures will be acquired from the Exploratory Studies Facility (ESF).

Required accuracy and precision and limits of methods

Based on current hydrologic estimates, the performance assessment of the site has a sufficient safety margin that accuracy requirements have not been established for geochemical retardation. The measurements to be performed are subject to accuracy and precision limits that can be considered normal for analytical chemical measurements.

Accuracy reflects the nearness of a measurement to its accepted value. Determinate errors are responsible for inaccurate results; their origin is due to personal errors of the experimentalist, instrumental errors, and methods of analyses. Determinate errors are either constant or proportional. In this study, most of the data consist of measuring the concentration of radionuclides or analogs to radionuclide species during elution through different types of columns. Concentration (C) consists of dividing the amount of radionuclide (as deter-

mined by an analytical technique) by the volume in which that amount of radionuclide was collected during elution. This eluted concentration is compared with the initial concentration (C_0) of the solution used for injection into the column. The analytical techniques and the experimental procedures used to determine the amount of radionuclide or analog in solution are given in Section 3.0 of the SCP (Study 8.3.1.3.6.1, Dynamic Transport Column Experiments). Prevention of determinate errors (which will cause inaccurate results) will be accomplished by analyzing standard samples from the National Institute of Standards Technology (NIST), running blanks, and varying the sample size analyzed. Proportional determinate errors will be identified and corrected by analyzing NIST standards. Constant determinate errors will be identified and corrected by analyzing NIST standards, blanks, and samples of different sizes. Consequently, we expect the measurements made in this study to be very accurate.

port experiments indicate that experiments (performed in duplicate) result in transport parameters with a precision of 20%.

Precision describes the reproducibility of results. Indeterminate errors are responsible for lack of precision in the experimental results. They arise from uncertainties that are unknown and cannot be controlled by the experimentalist. To calculate the accumulation of error in the quantity C/C_0 , which takes into consideration the precision of measuring volume as well as determining the amount of radionuclide in a given volume, one needs to consider the propagation of errors for multiplication and division. Thus, the relative standard deviation of the product C/C_0 is given by the square root of the sum of the squared relative standard deviations of the following: the volume in the original solution injected, the volume collected during elution, the amount of radionuclide in the volume injected, and the amount of radionuclide in the volume collected. The maximum relative standard deviation for the volume determination is 5%. The maximum relative standard deviation for the analytical techniques to be used for determination of the radionuclide amount is 10%. Consequently, the maximum relative standard deviation in C/C_0 is approximately 16%. The results of previous trans-

F. DIFFUSION STUDIES

Purpose and Objectives of Studies

Purpose

The goal of these studies is to experimentally determine diffusivities and mass transfer rates for consolidated tuff for use both in performance-assessment calculations and in support of the studies described in the Site Characterization Plan (SCP) for Study 8.3.1.3.6.2, Diffusion. The combined goal of this study and Study 8.3.1.3.6.1, Dynamic Transport Column Experiments, is to investigate the effective retardation of radionuclides by dispersive, diffusive, and advective processes. Specifically, Issue 1.1, Total System Performance, of the SCP needs experimental evidence that confirms or denies the theory of advective/diffusive coupling of solute concentrations in matrix and fracture flow. This theory is embodied in the transport model for fracture flow currently used in the transport model of TOSPAC described in Issue 1.1. Issue 1.1 states that information on advective/diffusive coupling is crucial in establishing the credibility of transport phenomenology embodied in any models used to assess the consequences of the release scenarios involving water pathways.

Use of results

This study will provide values for the effective diffusivity of aqueous chemical species contained in the pores of the matrix of each rock unit in the saturated and unsaturated zones needed for resolution of Issue 1.1. The parameter called for by Issue 1.1 is the empirical parameter measuring the effective diffusivity of the fracture matrix interface (constrictivity/tortuosity factor) for the saturated and unsaturated zones. An understanding of dispersal of radionuclides into the tuff matrix and the contributions of sorption to radionuclide retardation in an advective system is necessary to develop information on the parameters of Issue 1.1. The diffusion studies provide an additional means of measuring sorption and sorption kinetics. Issue 1.1 requires distribution coefficients for the rock matrix in both the unsaturated and saturated zones beyond the dis-

turbed zone. The bulk of the sorption data will be gathered in Investigation 8.3.1.3.4, Radionuclide Retardation by Sorption, but if these data are used in a dynamic system, sorption (distribution coefficients) must be evaluated in dynamic systems. The diffusion experiments will provide that evaluation and will support the use of the sorption data by Issue 1.1. The results of this study, however, will first be assessed by Investigation 8.3.1.3.7, Radionuclide Retardation by All Processes, before being used in Issue 1.1. The results from this study are also to be used in modeling and interpreting the experiments in Study 8.3.1.3.6.1, Dynamic Transport Column Experiments.

Rationale

Approach

We will study the migration of radionuclides and nonradioactive analogs of radionuclides through tuff samples under a variety of conditions. The experiments are intended to investigate the effects of the kinetics of sorption and diffusion on the liquid-phase transport of radionuclides. Current performance-assessment models assume instantaneous reaction rates. The kinetic data from the kinetics and diffusion studies will either support this assumption or will provide the data needed to more correctly model repository performance. Diffusivities are needed to predict the migration of radionuclides in fractured tuff. Diffusivity is also needed as a lower limit to transport rates for the matrix. The diffusivity in rock depends on pore structure. The measurements conducted in this study will determine the variability of pore tortuosity and constrictivity in Yucca Mountain tuff. To accomplish this, we have subdivided our efforts into the following activities.

- Diffusion studies will investigate the rate of movement of radionuclides through tuff in the absence of an advective flux. The processes of interest are molecular diffusion and sorption. These measurements will be performed using tuff disks of several thicknesses ranging from 1 to 5 cm because pumice grains of

about 1 cm may have a porosity and tortuosity in the pore structure different from porosity and tortuosity of the bulk tuff. If this is true, then thin slabs penetrated by these grains would yield a diffusivity that is not representative of the bulk rock. Thicker tuff disks are impractical because the time required to complete the experiments increases as the square of the thickness. The experiments designed will provide the necessary rock-dependent parameters, that is, tortuosity and constrictivity, for calculating the rate of diffusion of radionuclides through tuff and additional data on sorption distribution coefficients.

- Kinetics studies using solid tuff will provide kinetic rate constants by determining the time dependence of the uptake of radionuclides in solid tuff. These studies take advantage of the fact that diffusion-controlled uptake of dissolved species is linear versus the square root of time. If the sorption is influenced by kinetics, the observed uptake as a function of time will deviate from that controlled only by diffusion. To observe the effect of reaction rates on the uptake of radionuclides, the time required to diffuse through the solid must be short compared with the reaction time. Rapid reactions, such as ion exchange, can be studied by examining the uptake of radionuclides by thin wafers. Kinetic effects on ion exchange have been observed in 2-mm-thick tuff samples. The actinides, particularly americium, present special problems in the study of their sorption and kinetic properties. The actinides exhibit nonselective sorption on nongeologic materials, such as the walls of the sample containers. To overcome this inherent difficulty, the sorption of actinides will be studied as a function of time by using rock beakers so that the actinides will contact only the tuff.
- Unsaturated diffusion experiments will investigate diffusivity as a function of saturation in blocks of intact tuff. The diffusivity of radio-

nuclides is expected to decrease as the saturation decreases because the larger connections between pores will dry out first, which leaves a more tortuous path for radionuclides to migrate through. These studies will measure the change in the constrictivity/tortuosity parameter as a function of saturation. Small volumes of tracer will be injected into unsaturated tuff blocks in which the moisture distribution has been allowed to equilibrate for 0.5 to 2 yr. The tracer distribution after a diffusion period of 0.5 to 2 yr will be determined by sectioning the tuff blocks and measuring the concentration of radionuclides throughout the blocks.

Types of measurements to be made

The types of measurements will include tracer concentrations using 1) gamma-ray spectrometry, 2) liquid-scintillation counting, 3) alpha spectrometry, 4) scintillating-glass beta counting, and 5) ion chromatography. The porosity of rock matrices will be determined by measuring weight differences between saturated and dry samples. The analytical techniques used in these tests are standard techniques for this type of data acquisition.

Ancillary measurements will include bulk-rock mineralogy (described in the SCP for Investigation 8.3.1.3.2, Mineralogy, Petrology, and Rock Chemistry Within the Potential Emplacement Horizon and along Potential Flow Paths), tuff permeability, and batch distribution coefficients (described in Investigation 8.3.1.3.4, Radionuclide Retardation by Sorption).

Rationale for choosing the types of measurements to be made

The diffusivity of dissolved species in water can be calculated from ionic conductivities. The effective diffusivity of that aqueous species in rock depends on the porosity, the retardation factor, the tortuosity of the pore structure, and the constrictivity. Constrictivity is the result of the repulsion of the aqueous species by a charge on the mineral surfaces. The combined tortuosity/constrictivity factor can

be measured by observing the rate of diffusion through rock because ionic diffusivity, porosity, the distribution coefficient (K_d), and dry bulk density can be determined either by conducting an independent measurement or by reviewing the literature. The rate of diffusion will be observed by measuring the rate of movement of radionuclides through intact tuff in the absence of an advective flux. This method has been chosen because it is the closest simulation of the migration of radionuclides through tuff under the zero groundwater velocity limit. Another method for measuring tortuosity is to measure the electrical resistivity of rock, but this method cannot determine the conductivity.

Constraints on the study

One of the most significant constraints on this study is the extent of knowledge of potential transport pathways away from the repository. This constraint affects the selection of samples to be used for measuring diffusivity. Several samples from each unit will have to be tested to arrive at a measure of variability. In the absence of certain knowledge of what these pathways are, the lower and upper bounds on diffusivity obtained from this study will provide estimates of radionuclide transport.

Another constraint is the lack of knowledge of the chemical speciation of actinides and other multivalent elements under groundwater conditions at the proposed repository site. Investigation 8.3.1.3.5, Radionuclide Retardation by Precipitation, will address this limitation. Time will limit the scale on which the experiments can be carried out. The goal of achieving results within a few years limits the scale for nonsorbing tracers to about 10 cm. Sorbing tracers will be limited to a smaller scale because retardation will further slow diffusion.

Additional factors for consideration

Impact on site

The analyses necessary for this study should have minimal additional impact on the site because most samples necessary for the study will be obtained from core from existing and planned drill holes or

from surface outcrops. Large samples will be acquired from the exploratory studies facility (ESF).

Required accuracy and precision and limits of methods

Currently, the performance assessment of the site has a sufficient safety margin, based on hydrologic estimates, for us not to have established accuracy requirements for geochemical retardation. The measurements to be performed are subject to accuracy and precision limits that can be considered normal for analytical chemical measurements.

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